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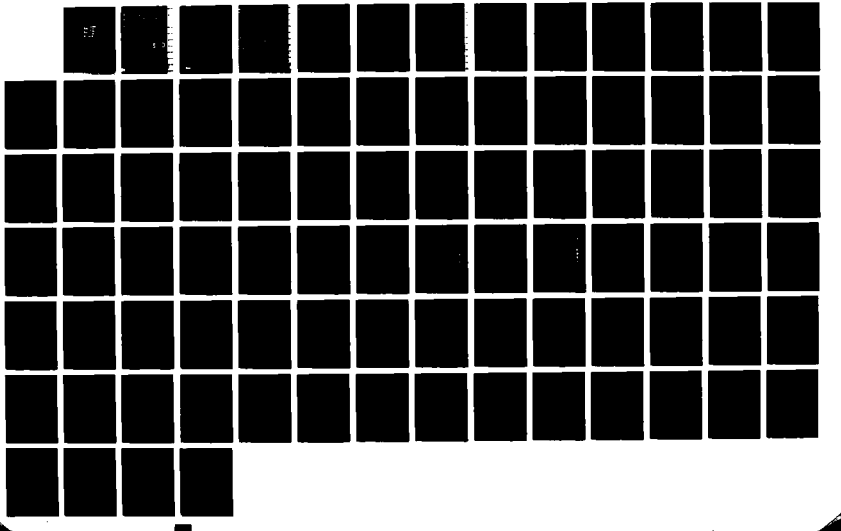

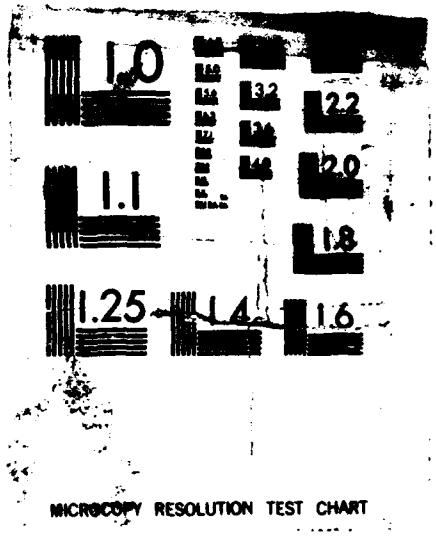
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ANALYSIS OF MIDDLE DISTILLATE FUELS BY HIGH RESOLUTION FIELD IONIZATION MASS SPECTROMETRY

May 1987

Final Report
Covering period June 1982 through November 1986

By: Ripudaman Malhotra, Michael J. Coggiola,
Steven E. Young, Doris S. Tse, and S. E. Buttrill Jr.

Prepared for:

NAVAL RESEARCH LABORATORY
Washington, DC 20375

Attention: Dr. Dennis R. Hardy
Code 6180

Contract No. N00014-81-K-2032

SRI Project PYU-3554

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Vice President
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We have developed an analytical method for the rapid and detailed chemical characterization of distillate fuels using high-resolution field ionization mass spectrometry (HR-FIMS). Field ionization produces only the molecular ions for most compounds and is therefore particularly useful for the analysis. A vintage AEI MS-9 mass spectrometer was refurbished and modified to house an SRI volcano-style field ionizer. By operating the mass spectrometer at a resolving power of 3000, all the hydrocarbon z-series present in the fuel can be resolved. Software was written for sorting the peaks according to their z-series, applying the appropriate response factors, printing and plotting the reports, and averaging replicate analyses.

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During this program, 26 different jet and diesel fuels supplied by the NRL were analyzed. For most cases, the analysis was straightforward, and meaningful atomic composition was obtained from the accurate mass data. In some examples, however, many peaks occurred at masses that did not correspond to meaningful atomic compositions. By choosing a different set of peaks for calibration, this problem was solved in some, but not all, cases. Most samples showed a wide range of components in the different z-series. Curiously, however, some samples had curiously very few peaks; they proved to be certain standard mixtures, instead of regular fuel samples.

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INTRODUCTION AND BACKGROUND

For the past several years, SRI International's unique field ionization mass spectrometer (FIMS) has provided detailed quantitative information on the composition of diesel and jet fuels derived from oil-shale, coal, and petroleum. Because field ionization (FI) is a very soft technique of ionization, it produces only molecular ions with very little fragmentation for most of the fuel components, and this makes analysis by FIMS relatively straightforward. Complete and quantitative molecular weight distributions of all the different types of hydrocarbon compounds present in these fuels previously required a time-consuming chromatographic separation of the fuel into several fractions. Each of these fractions was then analyzed separately by FIMS.

The objective of this current project (NRL Contract N00014-81-K-2032) was to develop a high-resolution FIMS (HR-FIMS) capability that would provide a detailed chemical analysis of fuels without prior chromatrographic separation.

A low-resolution mass spectrometer, which is capable of separating ions differing by a full mass unit, is not capable of resolving many of the different components present in a hydrocarbon fuel. Compound classes such as saturates and naphthalenes have the same nominal masses, but different molecular formulas and correspondingly different mass defects. Thus, for both nonane (C_9H_{20}) and naphthalene ($C_{10}H_8$), the molecular ions would result in a single peak at m/z 128 with a low-resolution mass spectrometer, but would appear as a doublet in a high-resolution instrument because the exact masses of these compounds are 128.1565 and 128.0626, respectively.

The resolving power ($M/\Delta M$) necessary to separate all saturates from the naphthalenes up to mass 300 is 3,200. The saturates/naphthalenes pair is one of the several examples of $C-H_{12}$ doublets. Others in this category include tetralins/pyrenes, tricycloalkanes/phenanthrenes. In all these pairs, the latter compound, which is of the same nominal mass as the former, has one more carbon and 12 fewer hydrogens. In each case, a resolving power of 3,200 is sufficient to resolve the doublets up to mass 300.

As the resolution of the mass spectrometer increases, minor components of a fuel containing heteroatoms such as oxygen, nitrogen, and sulfur can be separated, detected, and quantified. Table 1 shows the resolving power that is required to separate possible mass doublets at m/z 300, the molecular weight of the heaviest components expected in a middle distillate fuel. The mass doublets in Table 1 were selected as those most likely to be encountered in a field ionization mass spectrum, which consists almost entirely of molecular ions.

Table 1

RESOLVING POWER REQUIRED TO SEPARATE POSSIBLE MASS DOUBLETS AT m/z 300

Mass Doublet	$\Delta M \times 1000$	Required Resolving Power at m/z 300
$C-H_{12}$	93.9	3,200
$S-C_2H_8$	90.6	3,300
$O-CH_4$	36.4	8,200
$N_2-C_2H_4$	25.1	11,900
$S-O_2$	17.8	16,900
$^{34}SH^2-C_3$	16.5	18,200
$^{13}CO-N_2H$	15.7	19,100
$CO-N_2$	11.2	26,700
$^{13}C_2-C_2H_2$	8.9	33,600
$N-^{13}CH$	8.11	37,000
C_3-SH_4	3.37	89,000

Note: The resolving power tabulated is that necessary to separate two peaks of equal intensity such that the valley between them is 10% of their height. If one peak is very much smaller than the other, the resolving power required to quantitate the smaller peak increases by an amount that depends on the details of the mass spectometer peak shape.

The doublets are listed in decreasing order of mass difference or increasing values of the resolving power required to separate them. The separation of $S-C_2H_8$ doublet is only slightly more difficult than the separation of $C-H_{12}$ doublet, requiring a resolving power of 3,300. Another doublet involving sulfur, however, is much more difficult to separate: resolving power of 89,000 is required to separate the C_3-SH_4 doublet.

Nitrogen is the most abundant and most important heteroatom found in refined middle distillate fuels from shale. In a molecular ion spectrum, the $N-^{13}CH$ doublet will be encountered that requires 37,000 resolving power to separate at m/z 300. Increased resolution can be attained only at the expense of sensitivity. To date we have been operating the spectrometer at a resolving power of 3,000 because the focus of this study has been to resolve the different hydrocarbon series only.

This report describes the work performed during the period June 1982 to November 1986. Before this period, a used high-resolution mass spectrometer had been procured, refurbished, equipped with an SRI volcano-style field ionizer, and interfaced with a Kratos DS 55C data system for high-resolution mass spectrometry.

During this project, we developed a protocol for the analysis and have successfully used it to analyze many diesel and jet fuels. Molecular formulas are computed from the accurate mass data using the standard routine. Additionally, we have written software to sort and plot the peaks according to the number of carbons, n, and the degree of unsaturation, the z-number.

DESCRIPTION OF EQUIPMENT AND SOFTWARE

Each of the major elements of the HR-FIMS system used to analyze distillate fuels is considered separately in this section.

Field Ionization Mass Spectrometer

The mass spectrometer used in this work is an MS-9 manufactured by AEI, Ltd., of Manchester, England. It is a double-focusing mass spectrometer with 90-degree electric and magnetic sectors.

To install an SRI volcano-style field ionization (FI) source on the MS-9, the original source and mounting flange were removed along with the original solid sample probe and reentrant connection for the batch inlet system. A new housing, which includes provision for introducing solids via a heated direct insertion probe, was designed and installed.

The volcano-style FI source used in this project was designed at SRI by Aberth and Spindt.[1] [The ionizer is described in detail in the Final Technical Report (Contract N000173-79-C-0462) entitled, "Analysis of Middle Distillate Fuels by Field Ionization Mass Spectrometry."] Ions produced by the FI of fuel molecules are accelerated to 6 kV and focused into a narrow round beam. The ions then pass through a dual electrostatic quadrupole lens assembly that provides: strong focusing of the ion beam onto the entrance slit of the MS-9 mass spectrometer, and a means of transforming the round ion beam into a more nearly ribbon-shaped beam that better matches the shape of the entrance slit to the mass spectrometer.

The resolution of the MS-9 equipped with the FI source was tested with a mixture of hydrocarbons containing both saturates and naphthalenes in the molecular weight range of 128 to 156 amu. The instrument could easily resolve

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[1] W. Aberth and C. A. Spindt, Int. J. Mass Spectrom. Ion Phys., 1977, 25, 183.

the molecular ions of these two classes of compounds, indicating a resolution of greater than 1600. With a mixture of benzene and pyridine, we could resolve the molecular ions of pyridine and benzene containing a single carbon-13 atom; furthermore, the instrument was able to resolve the doublet due to the latter ion and the 1% of protonated benzene that is present in this system.[2] The separation of this minor ion from the molecular ion of benzene with one carbon-13 requires a resolving power of 18,800.

High-Temperature Batch-Inlet

The inlet system has been completely rebuilt and connected directly with the volcano-style FI source by means of a heated glass and quartz transfer line. The sample holder is sealed to the batch inlet using a gold gasket seal. This seal was not reliable and has allowed air to leak into the system on a few occasions. Careful polishing of all the mating surfaces has improved the performance considerably. The batch inlet can be operated up to 300°C, however, usually it is operated around 225°C, which is hot enough to get a normal signal for compounds as large as $C_{26}H_{54}$ (MW 366).

High-Resolution Mass Spectrometry Data System

The mass spectrometer has been interfaced with a Kratos DS-55C data system for control of the instrument as well as for data acquisition and processing. The system hardware consists of a NOVA-4C computer with a fast preprocessing board for rapid data acquisition, a Lear Siegler ADM5 monitor, a 12-Megabyte Winchester disk, and an 8-in floppy drive. The software package supplied by Kratos consists of an integrated and interrelated set of programs

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[2] R. Malhotra, M. J. Coggiola, S. E. Young, D. S. Tse, and S. E. Buttrill, Jr., "The Analysis of Middle Distillate Fuels by High-Resolution Field Ionization Mass Spectrometry," SRI International Annual Report, NRL Contract No. N00014-81-K-2082, 1984.

for the various aspects of high-resolution mass spectrometry. These include routines for:

- Control of the mass spectrometer
- Data acquisition
- Time-to-mass conversions
- Peak averaging
- Quantitation of peaks
- Plotting of spectra
- Computation of molecular formulas from accurate mass data
- Report production.

These routines were originally written for use with the electron-impact and chemical ionization modes. Most of them can be directly applied, however, even when the mass spectrometer is used with an FI source; only the routine for time-to-mass conversion requires some modifications in the way it is applied. The standard routine requires the presence of many reference peaks for calibrating high-resolution mass spectra. Normally, the reference peaks are produced by introducing perfluorokerosene (PFK) together with the sample into the FI source. Because of the negative mass defect of fluorine, the numerous fragment ions from PFK are easily resolved from the sample ions and can be used for calibration. FI, however, generally does not produce many fragment ions, and most of the commonly used reference mixtures, including PFK, are not suitable as internal mass references with FIMS.

Instead of adding compounds to provide reference peaks, we used some of the fuel components as mass references. For this purpose, we had to guess the exact masses of some of the peaks, and the entire procedure was one of boot-strapping. To facilitate the process of supplying different reference masses, we prepared many files containing accurate masses of various combinations of hydrocarbons. These files were used to provide the reference masses for the time-to-mass conversion routine. We found that the file containing accurate masses for alkylbenzenes works well for most fuels; however, in many instances, we had to use a different set of references to calibrate the spectrum.

In case the fuel sample does not contain components corresponding to some of the referenced masses, the calibration procedure can present some problems.

These problems emerge at two levels. First, if gross problems arise with missing reference masses, the resulting spectrum shows large regions with only nominal mass calibration. The other problem is more subtle and does not surface until the accurate mass data are converted into atomic compositions. In such cases, we observed a string of masses for which no meaningful composition could be calculated. In either case, we had to recalibrate the raw data using a different set of reference masses. On the other hand, when calibration is perfect, almost all of the peaks can be assigned reasonable atomic compositions. Figure 1 shows a portion of the report on atomic compositions for the various peaks obtained in the analysis of a diesel fuel marine sample (NRL 82-14). The list on the left with reference peaks at 168.0939 resulted in a narrow mass range of 57-176 and a string of "NONE" peaks, that is, peaks for which the data system could not calculate an atomic composition. Changing the reference peak to 168.1875 resulted in a different calibration over a wider mass range of 57-204, (shown on the right) that does not contain NONE peaks.

In addition to the software supplied by Kratos, we wrote some programs to perform certain tasks specific to fuel analysis. These tasks pertain to z-series analysis and are described below.

Software for Generating Z-Tables

Jet fuels are likely to contain anywhere between 50 and 150 components. A list of masses and their intensities would be a cumbersome way to present the information on the composition of these fuels. A more manageable representation would be a matrix in which homologous series of different compound classes are sorted into different columns. Because most of the fue components are hydrocarbons, the obvious choice of compound classification is according to the z-number, where z is defined by expressing the molecular formula of the hydrocarbon as C_nH_{2n+z}.

A mass scale that defines the mass of the CH_2 unit as 14.0000 has been used to sort the different compound classes because the mass defect of any given class in this scale will be the same throughout the mass range.[3] However, rather than writing a new computer code to generate a z-table from

DPO:1NR21O.MS NRL SAMPLE 82-14
NO. PEAKS: 38 REF PEAK AT 168.0939
MASS RANGE: 57.0703 - 176.1565

C	C13	H	S	DEV	MEAS MASS	#PTS	%INT	APPZ	TRUEZ
30	1		2						
13	0	12	0	-0.0	168.0939	17	54.38R	0	-14
13	0	11	0	-6.1	167.0800	12	11.89	-1	-15
12	1	10	0	-1.6				-1	-16
10	0	15	1	-9.5				-1	-5
9	1	14	1	-5.0				-1	-6
13	0	10	0	-3.7	166.0746	17	63.48	-2	-16
12	1	9	0	0.8				-2	-17
10	0	14	1	-7.0				-2	-6
9	1	13	1	-2.6				-2	-7
6	1	17	2	-6.0				-2	3
12	1	7	0	-13.5	164.0446	10	8.64	-4	-19
NONE					162.0768	12	10.45		
NONE					162.0268	14	14.88		
NONE					160.0710	12	14.06		
12	1	3	0	-12.3	160.0145	12	15.12	-8	-23
12	0	13	0	-12.2	157.0895	12	4.69	-11	-11
11	1	12	0	-7.7				-11	-12
8	1	16	1	-11.1				-11	-2
NONE					156.1533	14	15.79		
12	0	12	0	1.5	156.0954	14	16.68	2	-12
11	1	11	0	6.0				2	-13
9	0	16	1	-1.9				2	-2
8	1	15	1	2.6				2	-3
NONE					155.1464	10	4.65		
12	0	11	0	6.3	155.0924	12	10.83	1	-13
11	1	10	0	10.8				1	-14
9	0	15	1	3.0				1	-3
8	1	14	1	7.4				1	-4
NONE					154.1463	17	41.26		
9	0	14	1	13.8	154.0954	17	67.55	0	-4
NONE					153.1379	10	8.96		
NONE					153.0939	12	12.42		
10	1	19	0	-12.0	152.1400	17	52.55	-2	-3
NONE					152.1013	17	100.00		
NONE					150.1179	12	4.79		
NONE					149.1117	8	7.10		
11	0	16	0	0.0	148.1252	12	18.05R	-6	-6

DPO:1NR21N.MS NRL SAMPLE 82-14
NO. PEAKS: 42 REF PEAK AT 168.1875
MASS RANGE: 57.0703 - 204.1878

C	C13	H	S	DEV	MEAS MASS	#PTS	%INT	APPZ	TRUEZ
30	1		2						
12	0	24	0	-0.3	168.1875	17	68.91R	0	0
12	0	23	0	-4.2	167.1757	12	15.07	-1	-1
11	1	22	0	0.2				-1	-2
12	0	22	0	-0.9	166.1713	17	80.45	-2	-2
11	1	21	0	3.6				-2	-3
12	0	20	0	0.5	164.1570	10	10.95	-4	-4
11	1	19	0	4.9				-4	-5
12	0	18	0	-1.0	162.1399	14	16.35	-6	-6
11	1	17	0	3.5				-6	-7
12	0	16	0	-0.9	160.1243	12	18.58	-8	-8
11	1	15	0	3.6				-8	-9
9	0	20	1	-4.2				-8	2
8	1	19	1	0.2				-8	1
11	0	25	0	-6.1	157.1895	12	5.95	-11	3
10	1	24	0	-1.6				-11	2
11	0	24	0	-0.6	156.1871	14	20.56	2	2
10	1	23	0	3.8				2	1
11	0	23	0	-2.6	155.1774	12	10.59	1	1
10	1	22	0	1.9				1	0
11	0	22	0	-0.5	154.1716	17	70.77	0	0
10	1	21	0	3.9				0	-1
11	0	21	0	-4.8	153.1595	12	13.79	-1	-1
10	1	20	0	-0.3				-1	-2
11	0	20	0	0.2	152.1567	17	100.00	-2	-2
10	1	19	0	4.7				-2	-3
11	0	18	0	1.4	150.1423	12	6.07	-4	-4
10	1	17	0	5.9				-4	-5
11	0	17	0	-5.7	149.1273	8	9.00	-5	-5
10	1	16	0	-1.2				-5	-6
11	0	16	0	0.0	148.1252	12	22.88R	-6	-6

FIGURE 1 ATOMIC COMPOSITION REPORTS FOR FUEL NRL 82-14 SHOWING THE EFFECT OF MISASSIGNMENT OF REFERENCE PEAKS

The report on the left was generated using methyl biphenyl (168.0939) as one of the reference peaks. Reassigning the peak to a 12-carbon monocyclic saturate (168.1875) eliminated the problem of NONE peaks.

the raw data, we decided to modify an existing DS-55C program. A program for calculating the elemental composition corresponding to each peak in the spectrum already existed. We added a routine to it that calculated the z-number of each compound and sorted them accordingly. An added advantage of this approach is that the intensities of ^{13}C satellite peaks can also be easily added to the intensity of the parent peak.

As originally written, the DS-55C program used a combinatorial method to calculate all of the possible molecular compositions that would have an exact mass within some specified range about an experimentally measured mass. Thus, for a measured mass of 128.0643 (naphthalene), the program would determine that either $C_{10}H_8$ (with a deviation of 1.7 millimass units) or $C_9{}^{13}CH_7$ (with a mass deviation of 6.1 millimass units) was a possible elemental composition. If a heteroatom such as sulfur were included in the combinatorial search, then two additional compositions would be found: $C_7H_{12}S$ (-1.7 millimass units) and $C_6{}^{13}CH_{11}S$ (2.8 millimass units). Once these formulas are determined, the corresponding z-number is easily found as:

z-number = (number of hydrogen atoms) - 2 x (number of carbon atoms).

In this way, the first of the four compositions given above would yield z-numbers of -12, second -13, third -2, and fourth -3. On the assumption that the first elemental composition having an even z-number is the most likely choice, it is then a simple matter to enter the corresponding measured intensity into a table in which the rows are labeled by carbon number and the columns are labeled by the z-number. In the present case of naphthalene, the measured intensity of the peak at mass 128.0643 would be included in the table entry for carbon number 10, and z-number -12. A naphthalene molecule with a single ^{13}C substitution with a measured mass of 129.0674 would yield elemental compositions of $C_{10}H_9$ (deviation = -3.1 millimass unit, z-number = -11) and $C_9{}^{13}CH_8$ (deviation = 1.4 millimass units, z-number = -12). Because the ^{13}C composition has the even z-number, it would be assumed as the correct formula. Note that it too has a carbon number of 10 and a z-number of -12. Therefore, its intensity would be added to the intensity of the unsubstituted naphthalene already included in the table.

Software for Plotting Z-Series

We wrote a program, Z3PLOT, to draw 3-dimensional plots of the analyzed data of the z-series. The peak intensities are plotted against the carbon number for the different z-series. Figure 2 shows an example of such a plot using data for NRL fuel sample 81-11. The program uses two input parameters to adjust the output plot. The first parameter is the aspect ratio and the second is the angle. The aspect ratio controls the relative lengths of the "True Z" axis and the "Carbon #" axis. As the aspect ratio increases, the "True Z" axis is compressed relative to the "Carbon #" axis, thus allowing for more carbon numbers and fewer values. The angle parameter controls the rotation of the "Carbon #" axis relative to the horizontal ("True Z") axis.

Correction for Relative Field Ionization Efficiencies

Using standard mixtures, we previously measured the relative FI efficiencies, or sensitivity factors, of different hydrocarbon classes. These relative ionization efficiencies varied from 0.45 for acyclic saturates to 1.40 for naphthalenes and biphenyls. We have written a computer program that applies the appropriate sensitivity factor to the observed peak intensity and calculates the molar amount of the respective peak. Within a given z-series, the sensitivity also appears to vary somewhat with the length of the carbon chain. At present, however, we are applying the sensitivity corrections uniformly over a given series. In the future, we plan to measure the sensitivities for many more compounds and will be able to apply corrections as a function, not only of the z-series, but also the carbon number.

Miscellaneous Programs

To gain some knowledge regarding the reproducibility of the technique, we wrote a program that takes z-tables from replicate analyses and calculates the average intensity of each peak as well as the standard deviaton. The output has the format as that of a z-table, except that two numbers are at each location in the matrix; the upper number is the average intensity, and the lower number is the standard deviation. An example of this AVERAGE analysis of NRL 81-11 is shown in Table 2. As can be seen, the standard deviation for

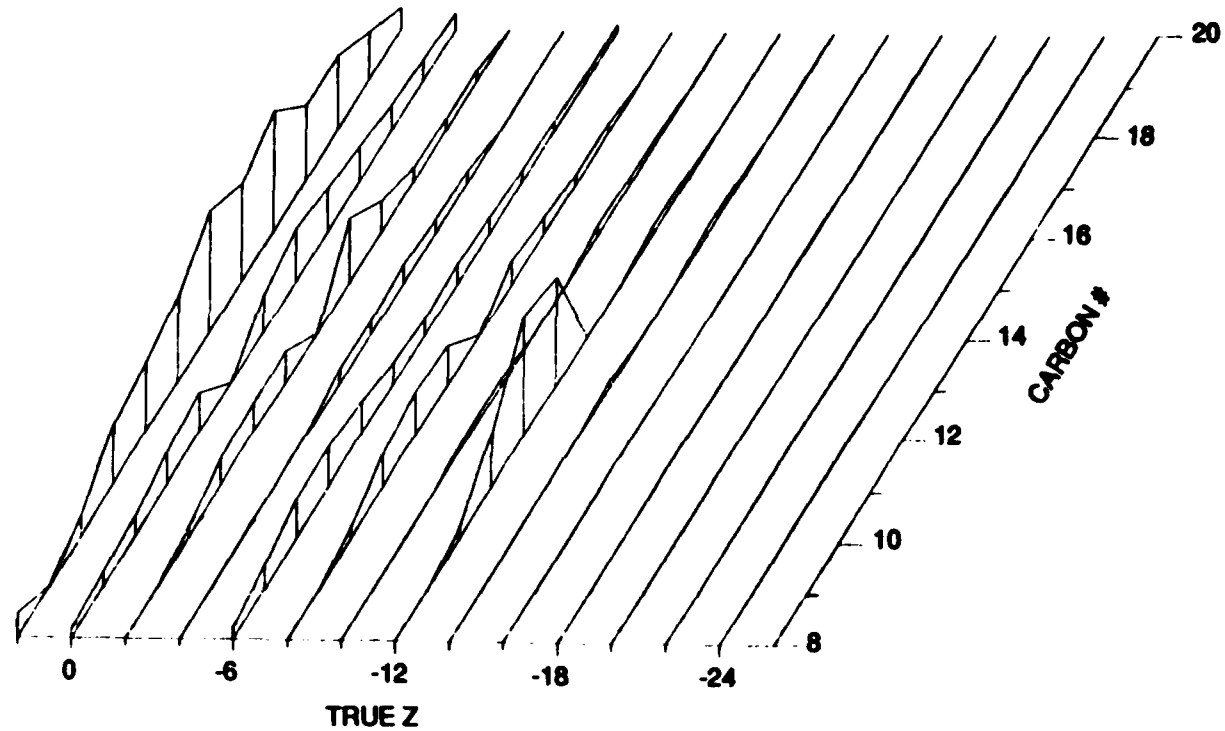


FIGURE 2 A 3-D PLOT SHOWING THE INTENSITIES OF VARIOUS COMPONENTS OF FUEL SAMPLE NRL-11 BY Z-SERIES

Table 2

AVERAGE OF FOUR ANALYSES OF FUEL SAMPLE NRL 81-11

AVERAGE OF THE FOLLOWING FILES: NRL SAMPLE 81-11
1NR4V.TB 2NR4V.TB 3NR4V.BB 4NR4V.TB

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.99	0.38	—	—	0.36	—	—	—	—	—	—	—	—	—
	—	—	—	—	0.10	—	—	—	—	—	—	—	—	—
9	—	0.47	—	—	1.00	—	—	—	—	—	—	—	—	—
	—	0.21	—	—	0.16	—	—	—	—	—	—	—	—	—
10	0.79	0.63	0.41	—	1.68	0.44	—	0.44	—	—	—	—	—	—
	0.13	0.18	0.02	—	0.25	0.08	—	0.03	—	—	—	—	—	—
11	1.82	1.02	0.81	—	1.84	1.45	—	2.54	—	—	—	—	—	—
	0.52	0.20	0.18	—	0.39	0.24	—	0.33	—	—	—	—	—	—
12	2.40	1.21	1.14	0.37	1.38	2.18	0.25	5.47	0.19	—	—	—	—	—
	0.46	0.33	0.19	—	0.17	0.47	—	0.60	0.02	—	—	—	—	—
13	3.38	1.38	1.16	0.56	1.08	2.09	0.35	4.66	0.35	—	—	0.15	—	—
	0.77	0.17	0.16	0.10	0.24	0.54	0.03	0.60	0.06	—	—	0.02	—	—
14	3.77	1.50	1.31	0.58	0.88	1.95	0.49	2.34	0.66	0.17	0.17	0.21	—	—
	0.96	0.07	0.10	0.05	0.26	0.41	0.06	0.32	0.13	—	—	0.03	—	—
15	3.86	1.56	2.30	0.67	0.91	1.22	0.55	0.96	0.59	0.19	0.24	0.18	—	—
	1.14	0.45	0.29	0.09	0.18	0.31	0.08	0.18	0.11	0.04	0.03	—	—	—
16	3.49	1.39	1.12	0.57	0.74	0.75	0.48	0.39	0.41	0.15	0.20	—	—	—
	1.25	0.31	0.13	0.04	0.14	0.11	0.07	0.03	0.07	0.00	0.05	—	—	—
17	2.27	1.03	0.55	0.44	0.55	0.46	0.36	0.26	0.24	—	—	—	—	—
	0.68	0.42	0.04	0.06	0.07	0.05	0.03	0.02	0.03	—	—	—	—	—
18	1.84	0.81	0.49	0.46	0.49	0.39	0.26	0.24	0.16	—	—	—	—	—
	0.90	0.22	0.08	0.15	0.08	0.02	0.07	—	0.02	—	—	—	—	—
19	1.43	0.68	0.43	—	0.33	0.31	—	—	—	—	—	—	—	—
	0.57	0.15	—	—	0.04	—	—	—	—	—	—	—	—	—
20	0.87	0.59	—	—	0.27	—	—	—	—	—	—	—	—	—
	0.30	0.11	—	—	—	—	—	—	—	—	—	—	—	—
SUM	26.92	12.66	9.71	3.66	11.52	11.24	2.73	17.29	2.61	0.51	0.60	0.54	—	—

*The upper number is the mole% of the component and the lower number is the standard deviation.

most peaks is less than 15%. During the current contract, we had to modify the mass spectrometer or the analysis scheme numerous times, consequently, we do not have replicate analyses that can be used to judge the reproducibility of the method.

In some fuel samples, several peaks were left unassigned even after we had tried different combinations of reference peaks. From the respective z-tables, we could often see what the assignment should have been. The recorded masses of these peaks, however, were too far from the expected values. To accommodate these peaks, we wrote a program to edit the z-table. This program allows the operator to intervene in the analysis; however, it should not be used routinely.

ANALYSIS METHOD

In general, the quantitative chemical analysis of a complex mixture requires the separation of that mixture by one or more means into individual components or groups of components. The amounts of each of the separated fractions or components are then determined. In earlier work, samples of jet or diesel fuels were separated using a liquid chromatographic procedure. Each of the chromatographic fractions was then analyzed further by gas chromatography, FIMS, or other means. The method being developed for this project is based on simultaneous separation and quantitation of fuel mixtures by HR-FIMS. The general procedure is described below.

Sample Introduction

Approximately 1-2 μL of liquid fuel together with 0.5-1 μL of a mixture of benzene, toluene, and isooctane, which serve as mass markers, are introduced into a high temperature, glass batch-inlet system attached to the HR-FIMS instrument. To minimize loss of volatile components during sample introduction, the fuel and the standard mass-marker mixture are taken in micropipettes (Microcaps, Drummond Scientific Company, Broomall, PA) and placed inside the sample holder. The sample holder is quickly immersed in a dewar containing liquid nitrogen to freeze the sample. The air in the sample holder is pumped out, opening the connection to the evacuated batch inlet. The liquid nitrogen dewar is then removed and a small oven (at ca. 200°C) is placed around the sample holder to completely evaporate the sample. The sample vapors expand into the batch inlet from where they flow into the source through a small leak. Because all of the fuel sample is vaporized at the same time, the number of molecules of a specific type flowing into the ion source is directly proportional to the number of molecules of that type present in the original fuel.

Ionization and Data Acquisition

The FI source in the mass spectrometer ionizes sample molecules into molecular ions. The molecular ions are separated according to their masses by the spectrometer, which is operated at a mass resolution of 3000 or greater, sufficient to completely separate the molecular ions of the different hydrocarbon types present in the original fuel. The mass spectrometer is scanned at a speed of 120 s per decade. A scan time of 110 seconds plus a magnet settling time of 10 s allows one scan to be completed every 2 min. Typically, 10 scans are collected, although the amount of sample used is sufficient to allow two to three times as many scans if so desired.

A mixture of benzene, toluene, and isooctane is added to the fuel sample. Isooctane is one of the few compounds that even under FI undergoes complete fragmentation to give t-butyl ions. This is advantageous because the molecular ion of isooctane would be in the mass range of interest. At the same time, isooctane boils at a high enough temperature to allow easy handling. The fragment t-butyl ion produced from isooctane and the molecular ions of benzene and toluene serve as the autostart masses for the time-to-mass conversion software.

Time centroid data are usually collected because they can be conveniently reprocessed in the event of an incomplete or unsatisfactory time-to-mass conversion. As discussed in the previous section, (p. 7), calibration of the HR-FIMS can sometimes be a problem because of the highly variable fuel composition of distillate fuels from different sources. Reprocessing of the time-centroid data with a different set of reference peaks is necessary in such cases.

Calibration Reference Files

We created a series of reference files using different classes of hydrocarbons, such as acyclic saturates (SAT), alkylbenzenes (RBZ), naphthalenes (NAP), or combinations of two classes of compounds--for example, alternating the saturates with alkylbenzenes (SATRBZ) and the monocyclic saturates with biphenyls (U1BP). We applied these files to the uncalibrated spectra of various fuel samples. We found that because of the large variability in the composition of different fuels, no unique calibration file is good for all of

them. We have to test the different calibration reference files with each fuel. In general, the extent of the mass range that is accurately calibrated and the number of NONE peaks are good indicators of the quality of calibration. Our attempt is to calibrate the widest possible mass range and have the minimum number of NONE peaks. We found that for most fuels the reference file containing accurate masses of alkylbenzenes (RBZ) works better than the other reference files.

Data Processing

Each of the scans of ion peak intensity is stored in a computerized HR-FIMS data system that averages these individual scans and calculates the accurate masses and the elemental composition (chemical formulas) of each of the peaks in the FI mass spectrum of the fuel sample. This information enables the peak intensities to be sorted by compound type (z-series) and by the number of carbons present in the molecule. The final result of the analysis is a table showing the relative amounts of the various compounds present in the fuel mixture, organized by z-series and carbon number. The relative FI signals of each component of the fuel can be converted into mole fraction of that component present in the original fuel sample by using measured relative FI efficiency data for known compounds.

RESULTS OF FUEL ANALYSIS

During the course of this study, 26 fuel samples were analyzed by HR-FIMS. The fuel samples are identified by their NRL designation. On receipt at SRI, the samples were also given an SRI indentification number. Table 3 gives the number of NONE peaks in each of the analyses as well as summary results of the analysis in terms of mol% total acyclic alkanes, naphthenes, monoaromatics, and polyaromatics. Plots and z-tables for all the samples are included in the appendix.

Most samples show a complex pattern of peaks with homologous series corresponding to different z-values. A few samples do not fit this pattern and have either too few peaks or have peaks restricted to a couple of z-series only. For example, Sample 81-21 has very few peaks and > 98.7 mol% of monoaromatics. It turns out that this sample is a xylene-bottoms sample. Similarly, Sample 82-12, with about 83% acyclic saturates, is a Koppers mixed naphtha.

Table 3

SUMMARY OF HR-FIMS ANALYSIS OF 26 NRL FUEL SAMPLES

SAMPLE	NRL #	RUNNAME	# NONE PEAKS/ # TOTAL PEAKS	ACYCLIC	NAPHTHENES	MONOAROMATICS	POLYAROMATICS
1	81-8	4NR1Z	108/166	29.2	31.5	29.4	9.9
2	81-9A	3NR2V	0/127	15.0	42.4	34.0	8.6
3	81-10	2NR3V	32/180	25.9	19.4	23.9	30.8
4	81-11	3NR4V	0/101	22.5	25.5	29.8	22.2
5	81-12	2NR5V	0/72	30.0	33.8	23.7	12.6
6	81-13	2NR6V	0/123	16.1	20.8	50.6	12.5
7	81-14	1NR7V	0/114	17.5	26.4	33.1	23.0
8	81-15	2NR8V	0/81	29.4	29.8	34.1	6.7
9	81-16	2NR9V	0/94	32.7	35.2	26.4	5.7
10	81-17	2NR10W	32/131	11.2	26.3	44.0	18.5
11	81-18	2NR11P	2/88	8.8	25.6	41.6	24.0
12	81-19A	4NR12V	10/93	10.0	31.0	33.5	25.5
13	81-20	2NR13P	32/55	39.8	32.8	26.6	0.8
14	81-21	2NR14M	11/44	0.5	0.7	98.7	0.1
15	81-22	2NR15P	0/79	27.5	32.7	25.6	14.1
16	81-24	2NR16Z	44/75	63.2	4.7	21.3	10.8
17	81-25	2NR17R	47/81	29.6	36.1	20.7	13.6
18	82-10	2NR18Q	64/215	13.5	29.6	26.4	30.4
19	82-12	4NR19Z	22/40	83.1	0.6	6.4	9.9
20	82-13	2NR20Z	52/96	48.2	1.7	50.0	0.1
21	82-14	1NR21T	0/45	18.7	70.6	10.7	0.0
22	82-15	3MR22V	2/222	15.3	34.3	30.5	19.9
23	82-17	1NR23W	49/66	45.3	20.1	29.3	5.3
24	82-33	3NR24P	95/181	15.0	30.5	36.2	18.3
25	83-7	7NR26Q	84/119	23.1	24.2	29.5	23.2
26	83-14	1NR27V	20/135	27.8	20.6	30.7	20.9

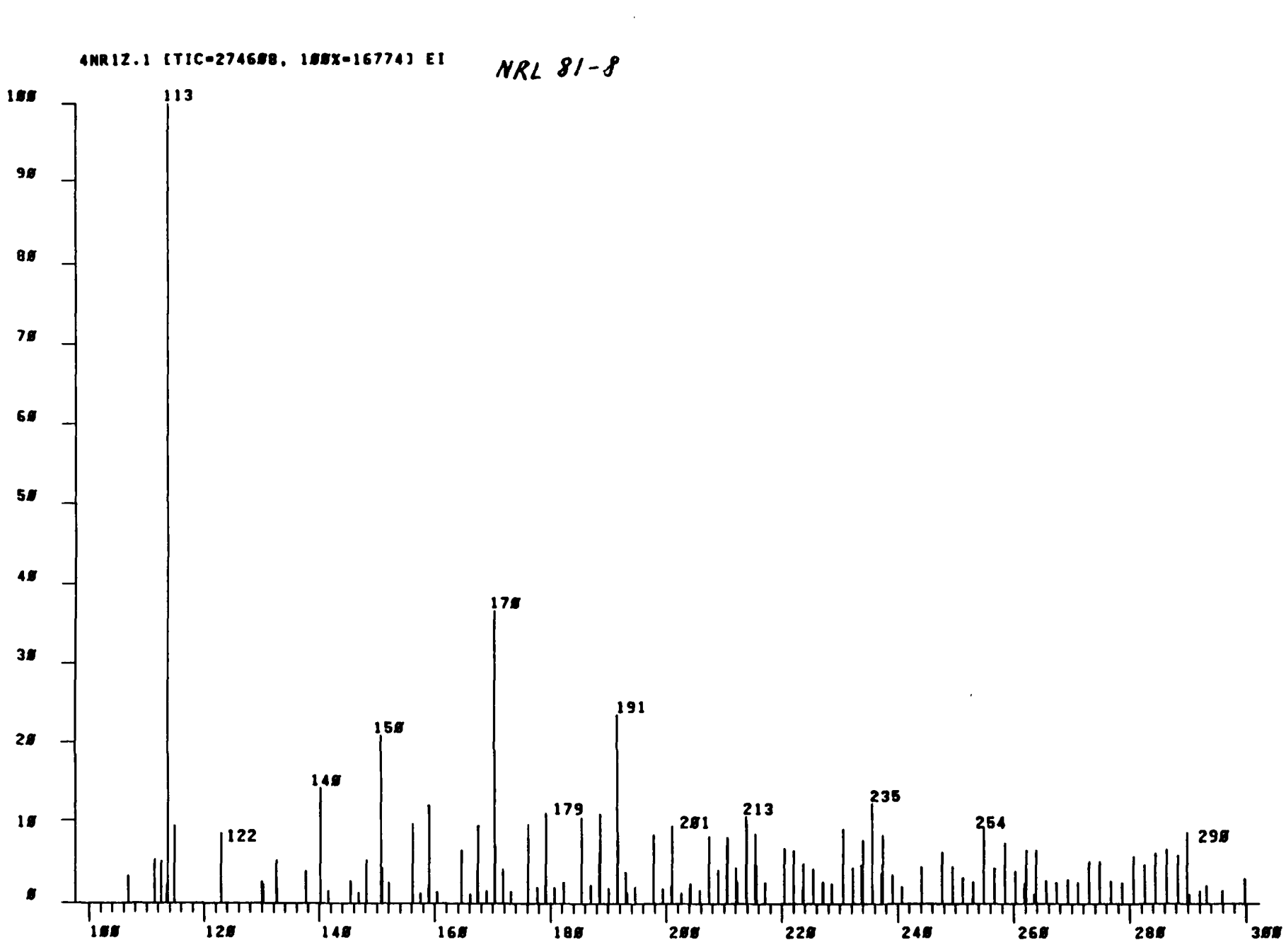
FUTURE STUDIES

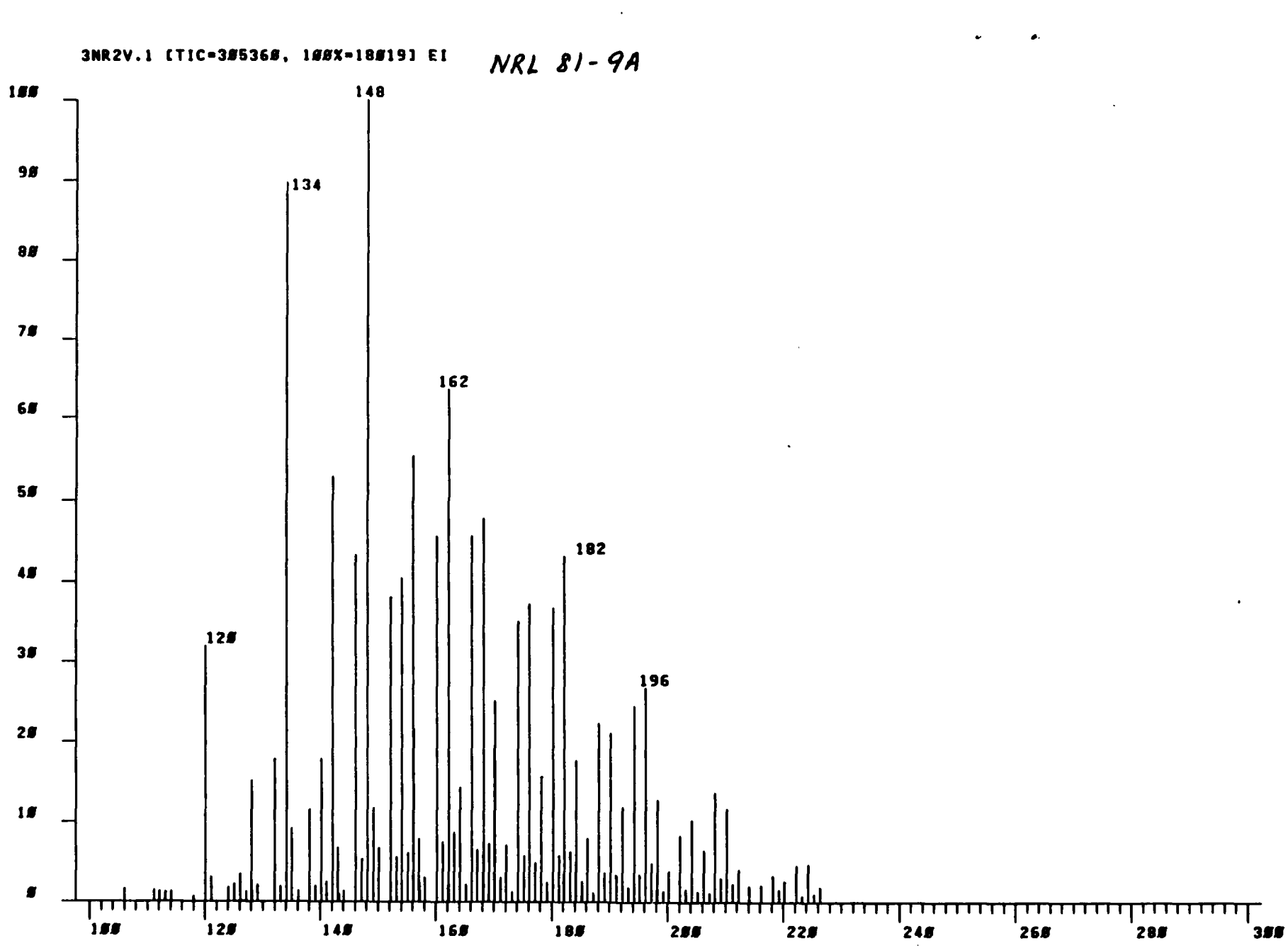
One of the goals of the HR-FIMS analysis is to provide composition-property relations. The detailed chemical composition provided by HR-FIMS is ideal for exploring correlations between bulk properties and composition through various statistical analyses. Before performing such regression analyses, however, we have to determine the degree of reproducibility and repeatability of FIMS analysis. During this study, we could perform only short-term reproducibility tests on a few samples. The results are encouraging; most peaks showed a standard deviation of less than 10%. The generality of such reproducibility, however, is yet to be demonstrated.

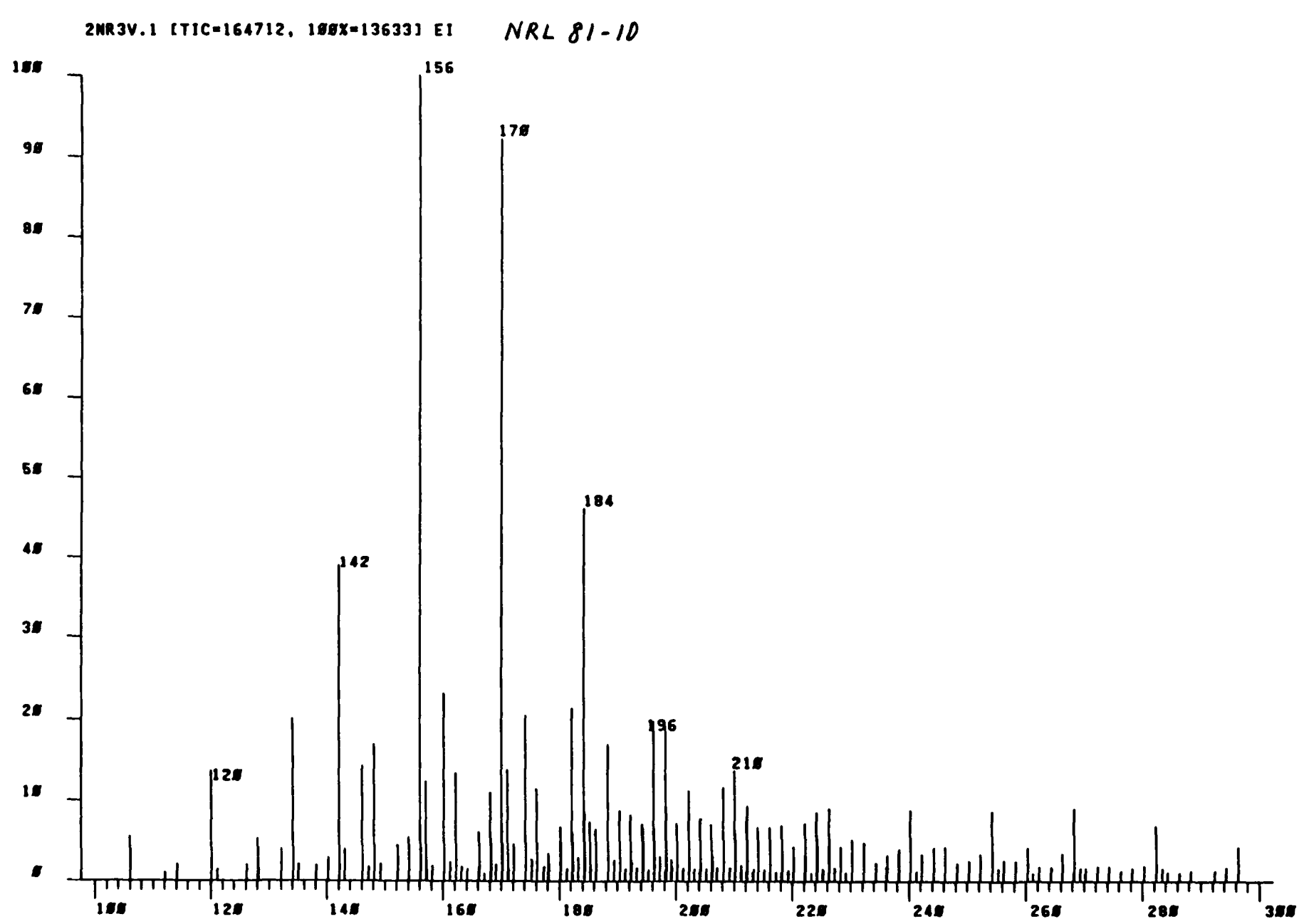
We also noticed a difficulty with the batch-inlet system. The procedure for securing the sample holder to the rest of the inlet with a nut often results in some leaks despite the use of gold gaskets. Moreover, these leaks are not noticed until after the freeze-pump cycle, and by then, some of the volatiles may be lost. The glass-ball valves in the batch inlet also do not seal perfectly and are a source for potential selective loss of the more volatile components. We believe that replacing the batch-inlet system with a more reliable one would help increase the reproducibility of the technique.

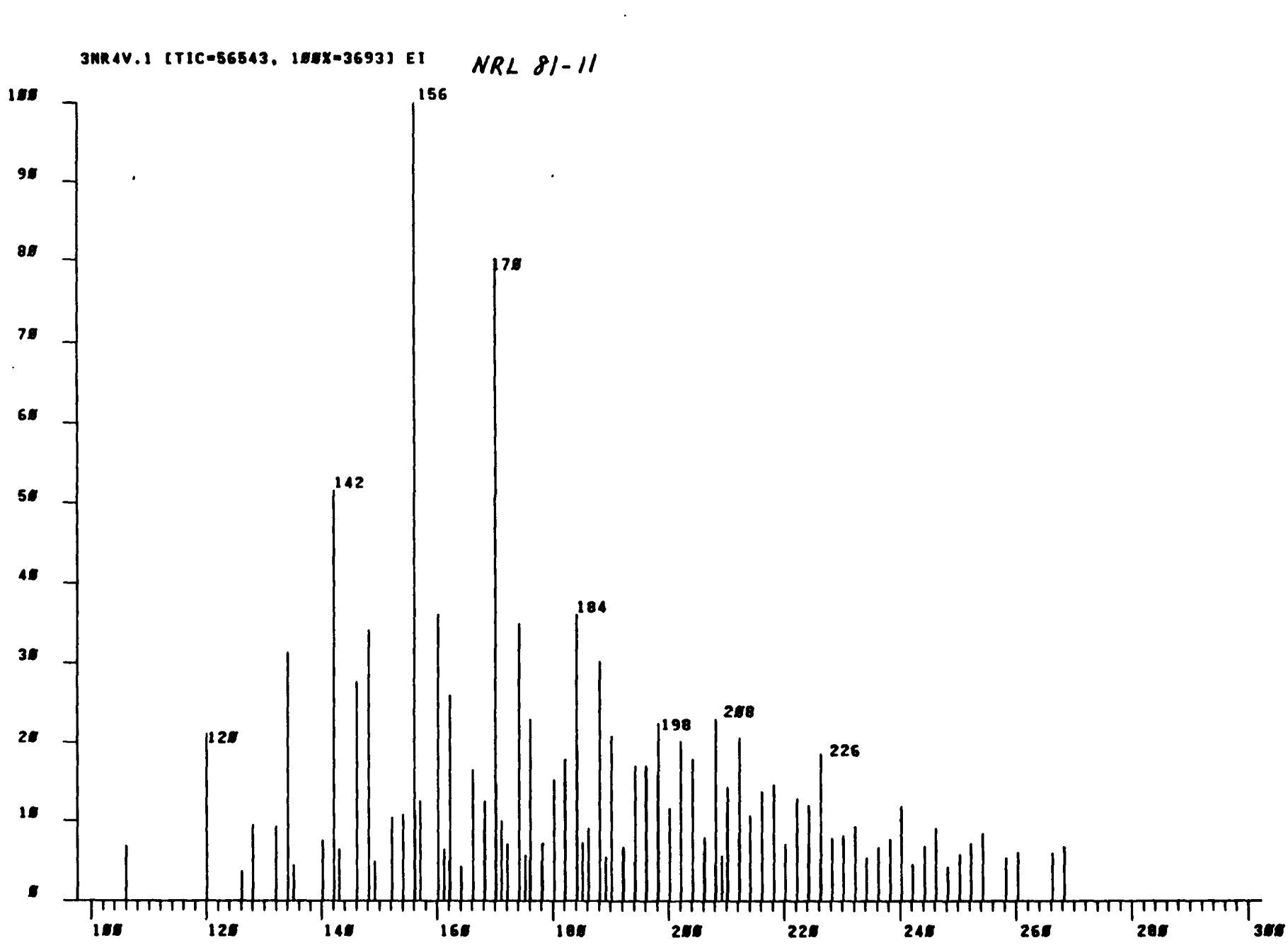
Appendix

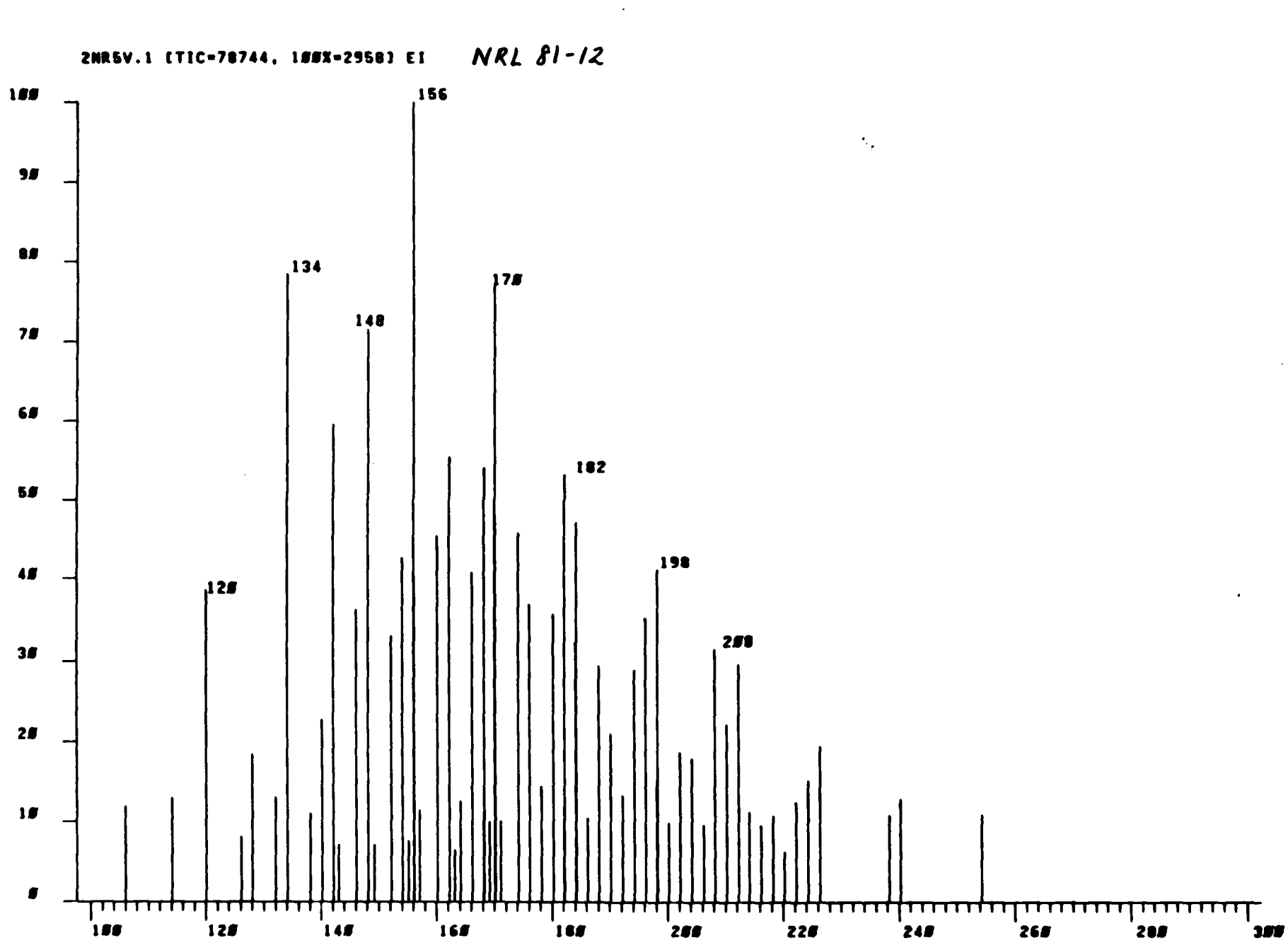
RESULTS OF HR-FIMS ANALYSIS OF MIDDLE DISTILLATE FUELS SUPPLIED BY THE NAVAL RESEARCH LABORATORY: COLLECTION OF PLOTS AND z-TABLES


4NR1Z.1 [TIC=27468#, 1##X=16774] EI
NRL 81-8
1##
9#
8#
7#
6#
5#
4#
3#
2#
1#
#
113
122
14#
15#
17#
179
191
2#1
213
235
254
29#
1#
12#
14#
16#
18#
2##
22#
24#
26#
28#
3##


3NR2V.1 [TIC=3#536#, 1##X=18#19] EI
NRL 81-9A
148
134
162
182
196
128
100
90
80
70
60
50
40
30
20
10
0
100
120
140
160
180
200
220
240
260
280
300


2NR3V.1 [TIC=164712, 100%=13633] EI
NRL 81-10
100
90
80
70
60
50
40
30
20
10
0
156
170
184
142
196
210
120
100
120
140
160
180
200
220
240
260
280
300


3NR4V.1 [TIC=56543, 100%=3693] EI
NRL 81-11
100
90
80
70
60
50
40
30
20
10
0
156
173
142
184
198
208
226
120
100
120
140
160
180
200
220
240
260
280
300


2NR5V.1 (TIC=78744, 100%=2958) EI
NRL 81-12
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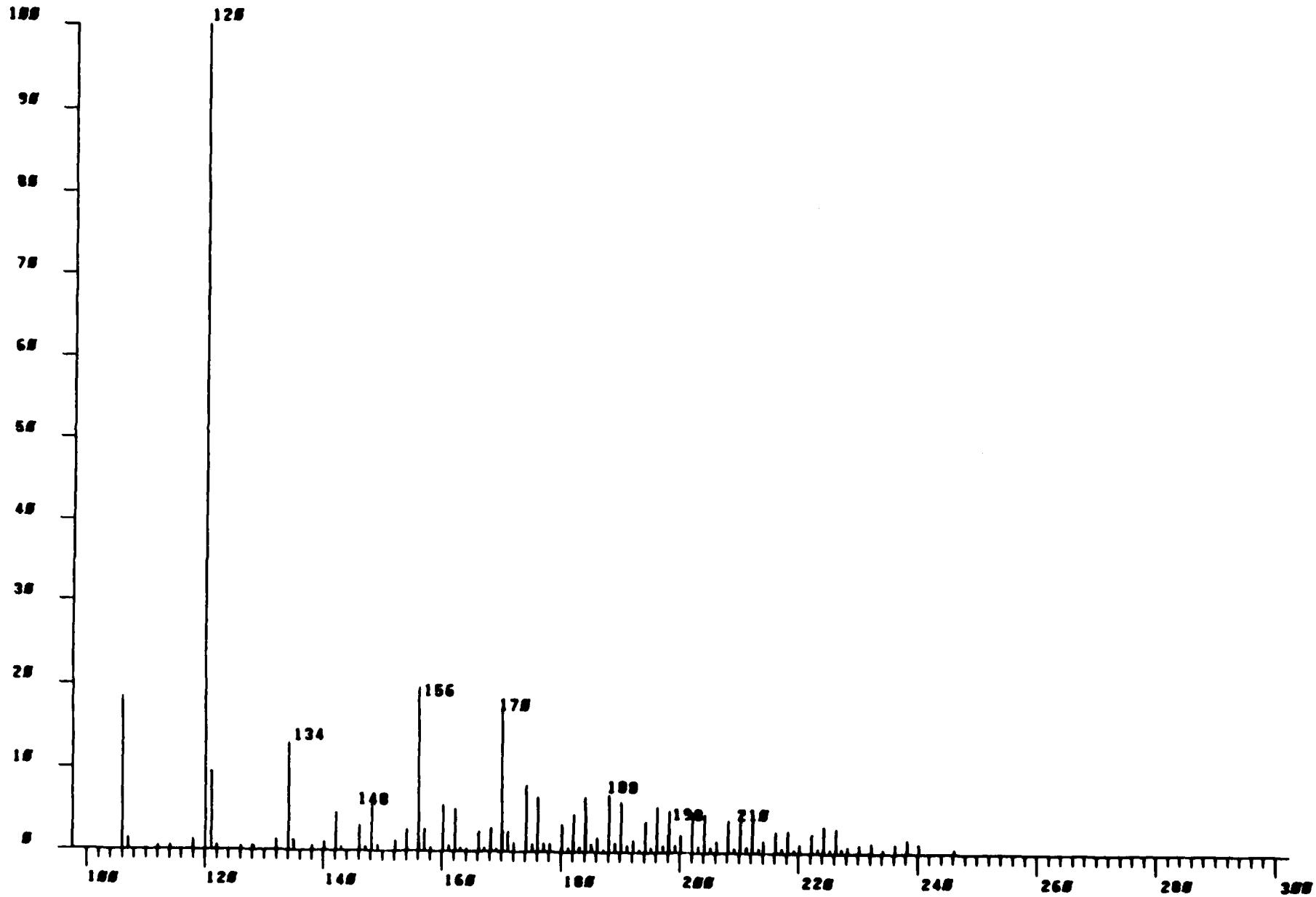
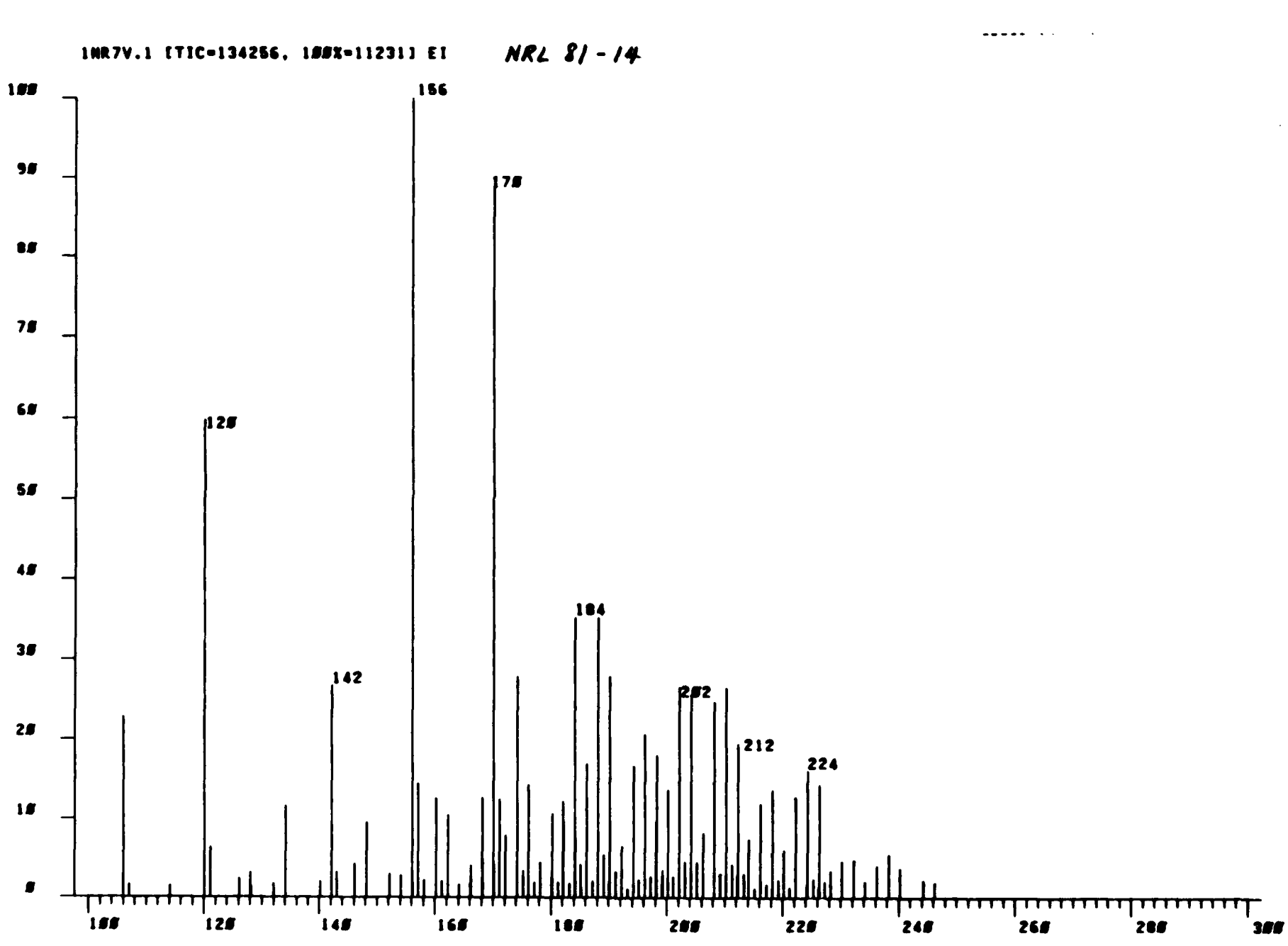
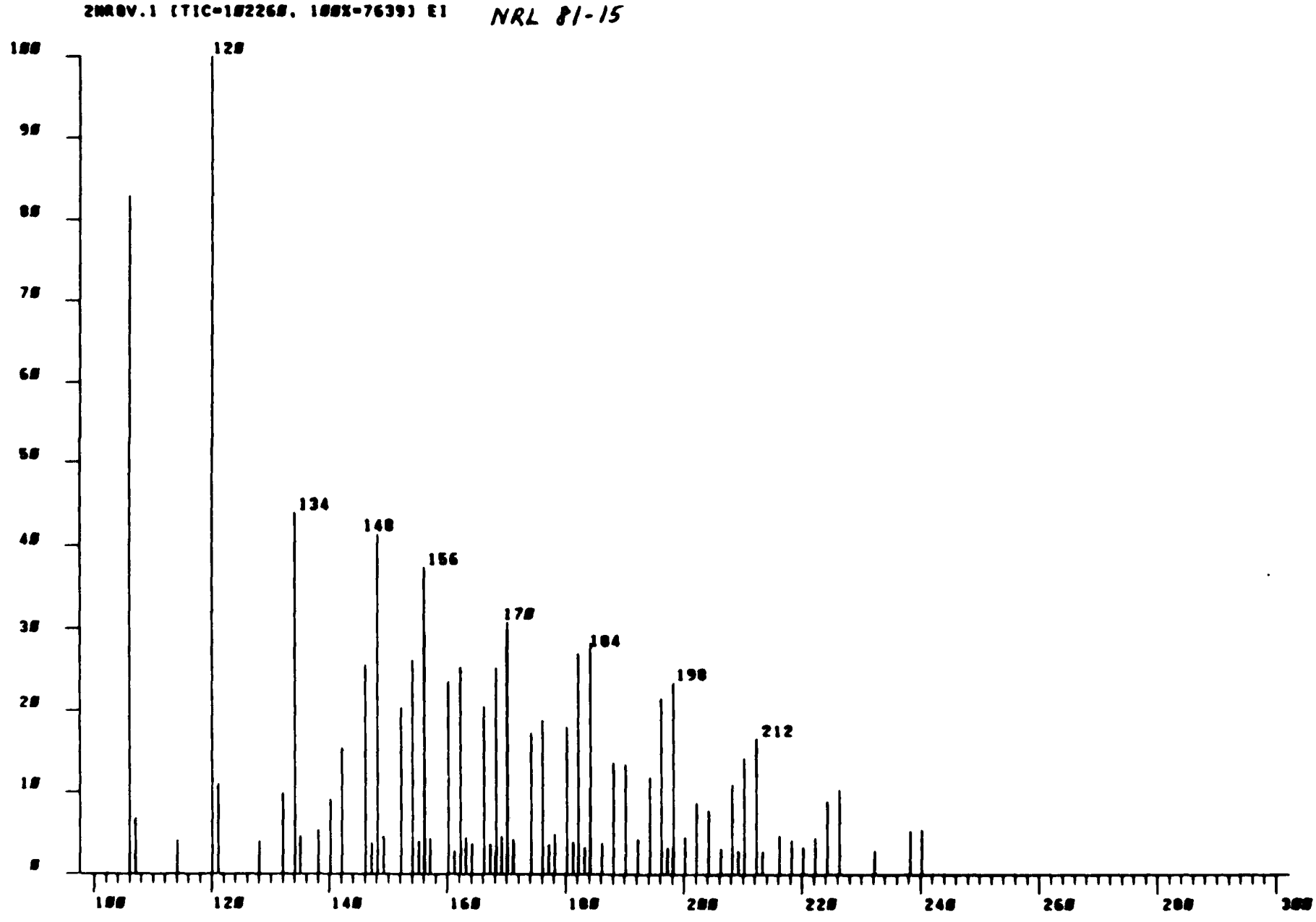
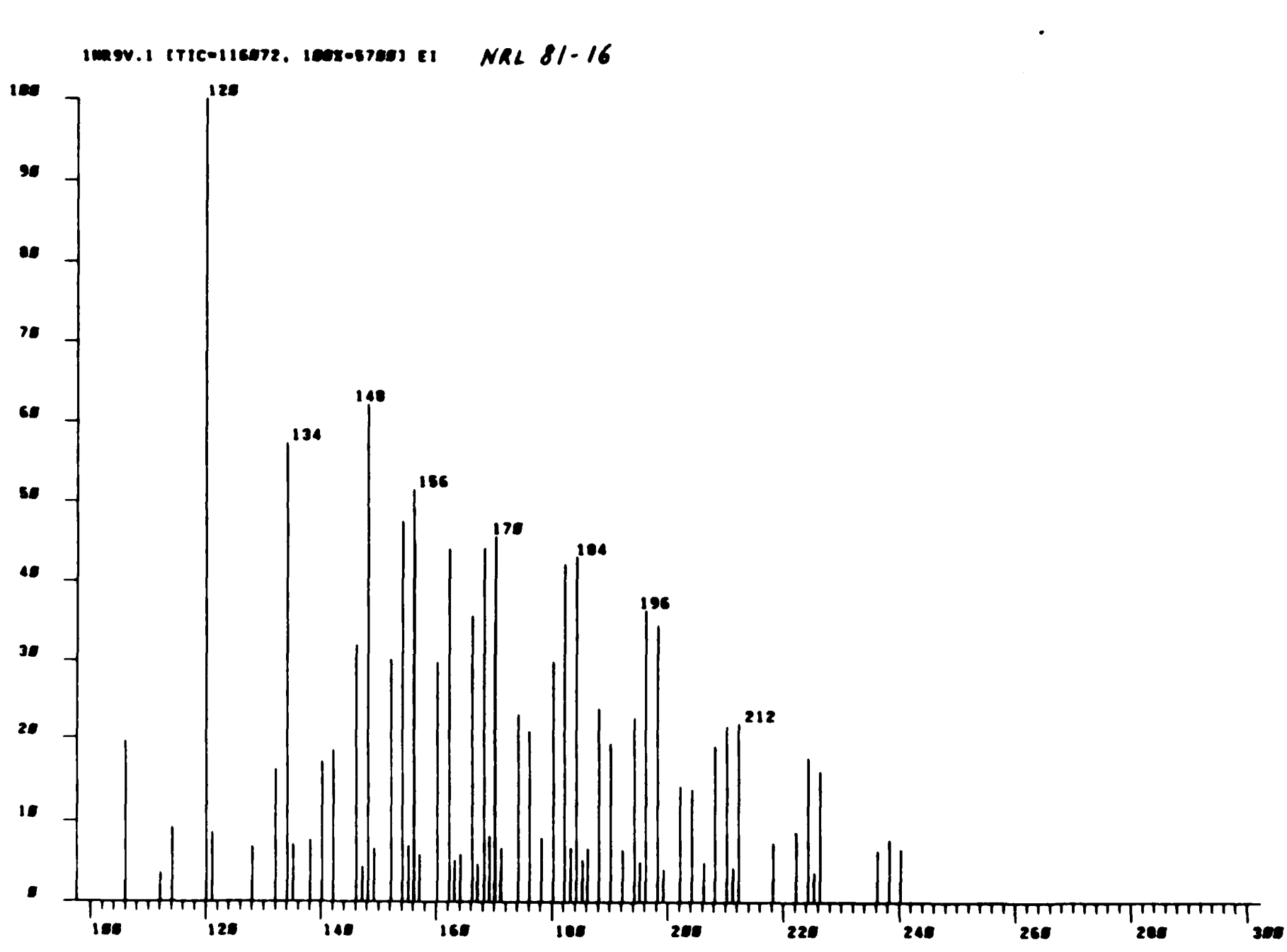
80
70
60
50
40
30
20
10
0
156
134
148
170
182
198
120
200
100
120
140
160
180
200
220
240
260
280
300

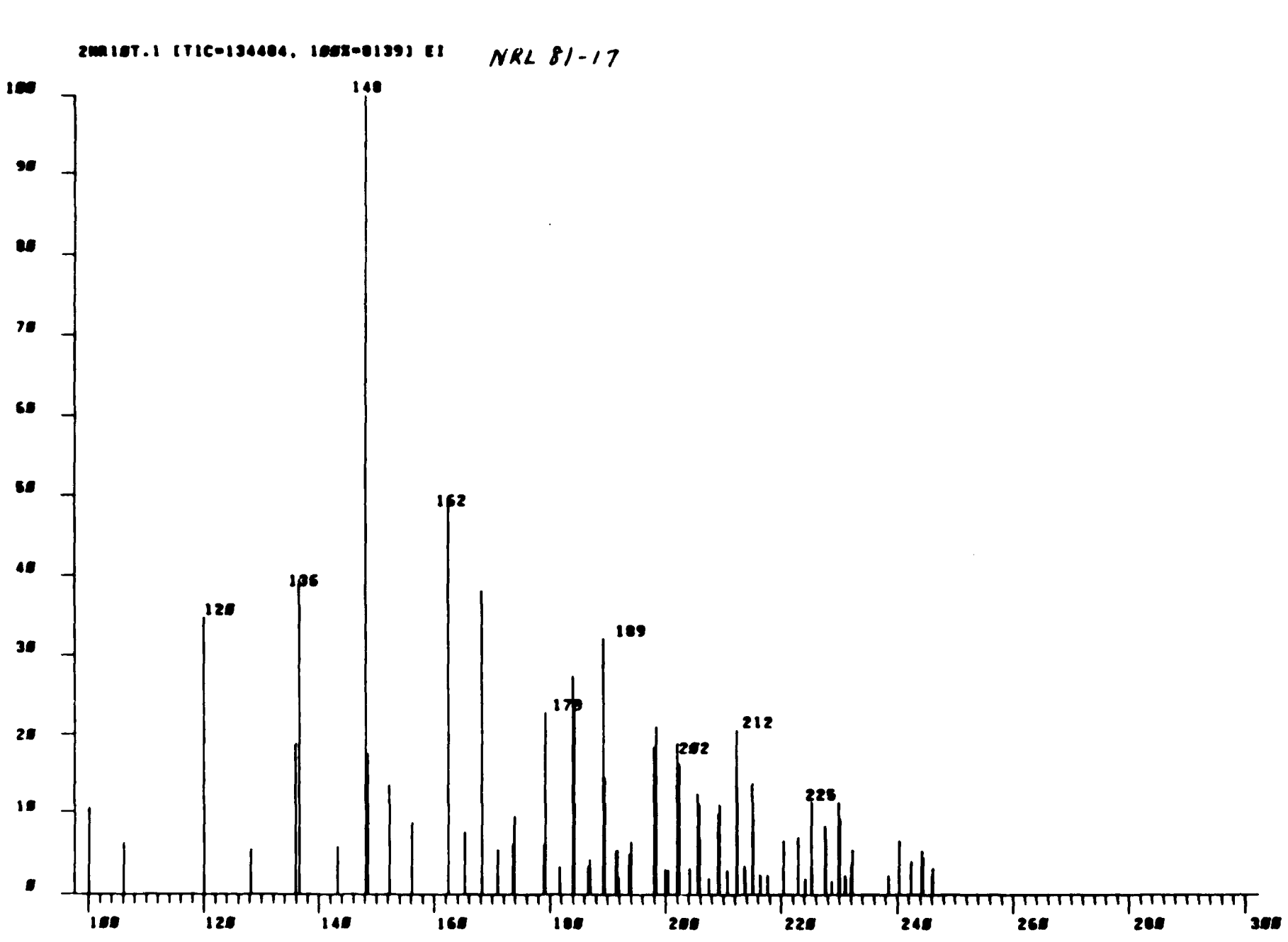
2HR6V.1 [TIC=176156, 100%=41868] EI NRL 81-13

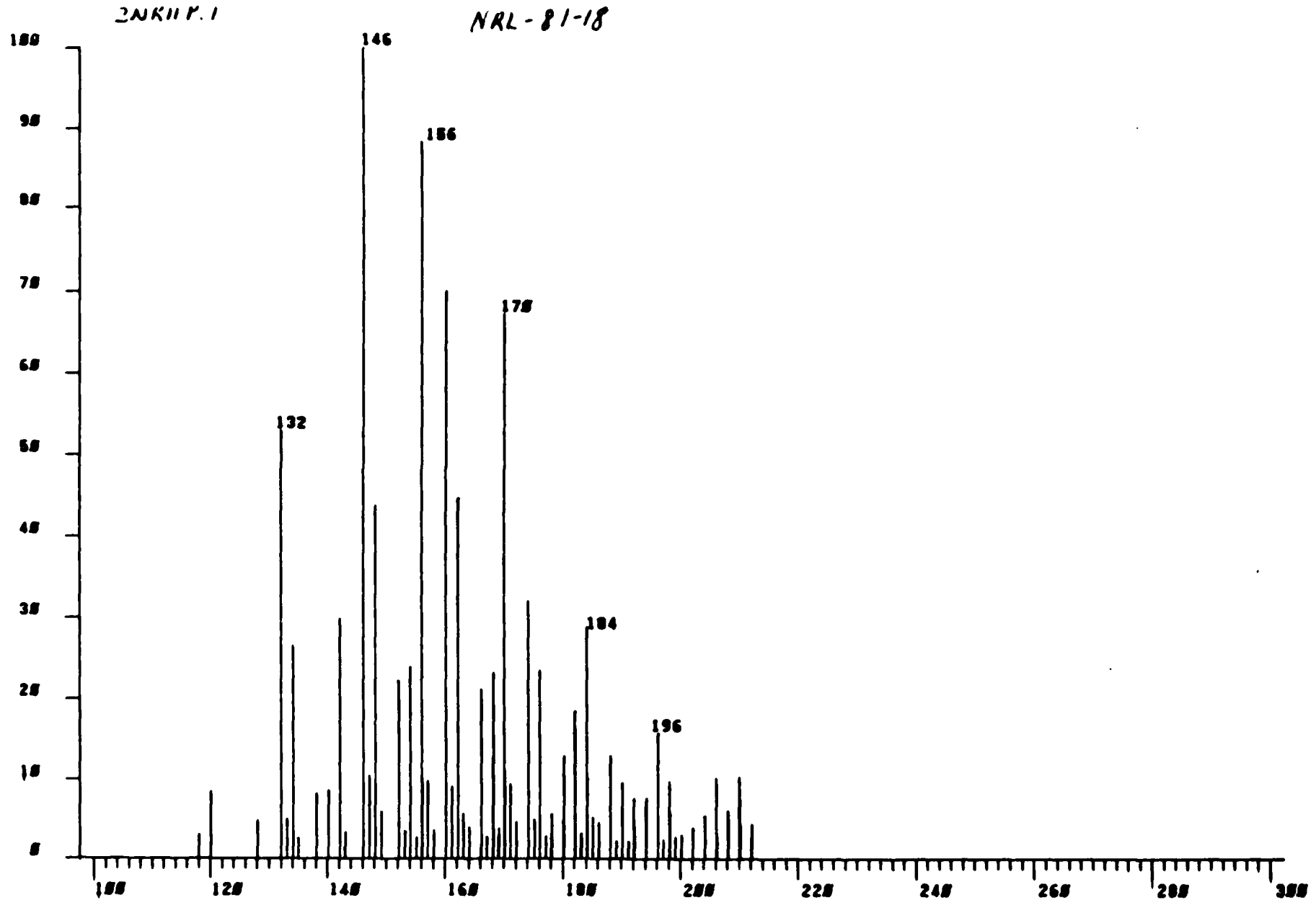



1NR7V.1 [TIC=134256, 100%=112311] EI
NRL 81-14
100
90
80
70
60
50
40
30
20
10
0
166
178
128
184
142
202
212
224
100
120
140
160
180
200
220
240
260
280
300


2NR8V.1 (TIC=182268, 188%=7639) EI
NRL 81-15
100
90
80
70
60
50
40
30
20
10
0
128
134
148
156
170
184
198
212
100
120
140
160
180
200
220
240
260
280
300


1MR9V.1 (TIC=116872, 100%=57800) EI
NRL 81-16
100
90
80
70
60
50
40
30
20
10
0
128
134
148
156
178
184
196
212
100
120
140
160
180
200
220
240
260
280
300


2MR18T.1 [TIC=134484, 100%=8139] EI
NRL 81-17
148
162
136
128
189
179
212
202
225
100
90
80
70
60
50
40
30
20
10
0
100
120
140
160
180
200
220
240
260
280
300


ZNKII P. 1
NRL-81-18
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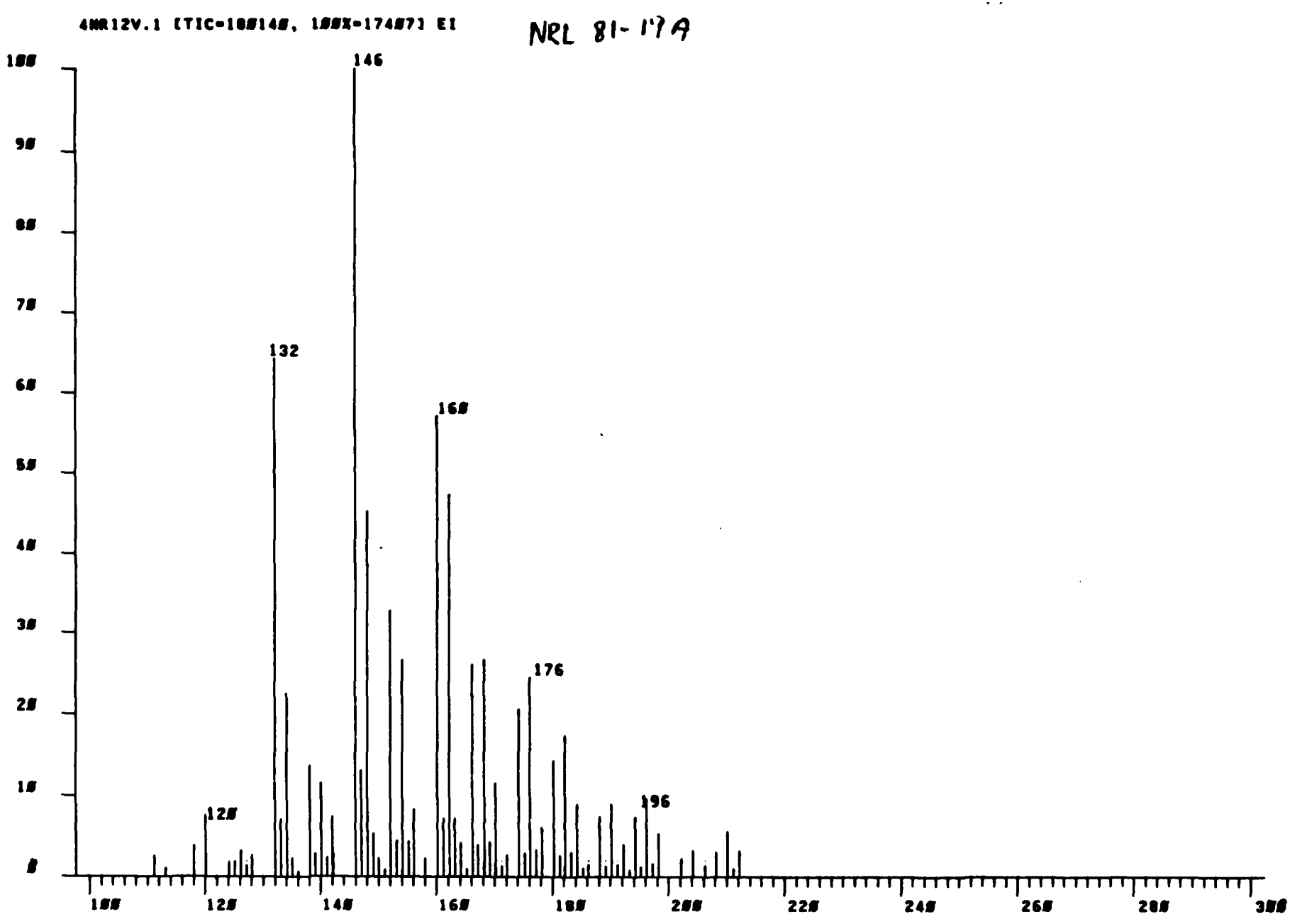
90
80
70
60
50
40
30
20
10
0
146
156
178
132
184
196
100
120
140
160
180
200
220
240
260
280
300


4NR12V.1 [TIC=18814#, 188X=174871 EI
NRL 81-17A
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90
80
70
60
50
40
30
20
10
0
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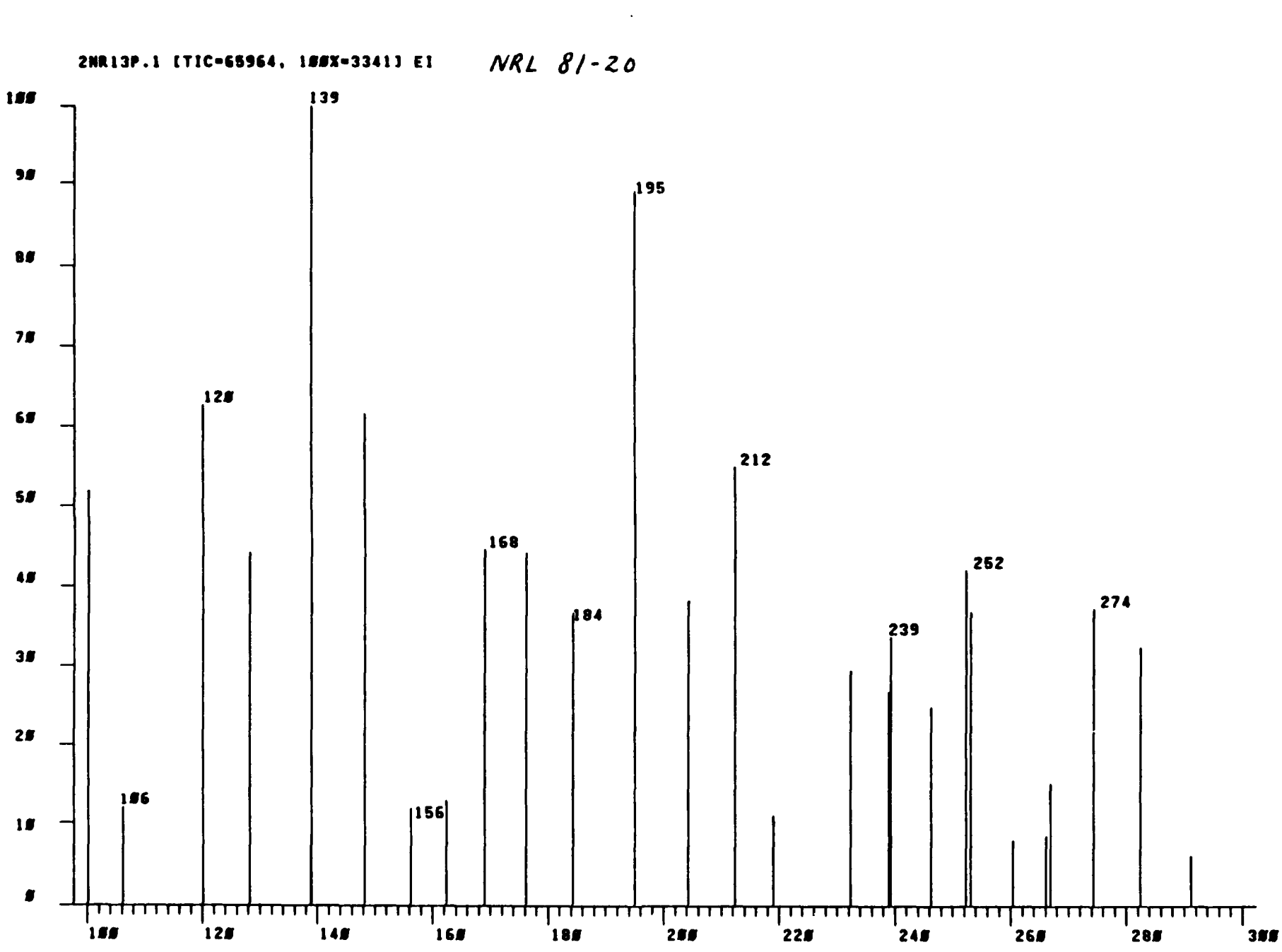
132
168
176
196
128
100
120
140
160
180
200
220
240
260
280
300


2NR13P.1 [TIC=65964, 100%=3341] EI
NRL 81-20
100
90
80
70
60
50
40
30
20
10
0
139
195
128
212
168
252
184
274
239
156
106
100
120
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160
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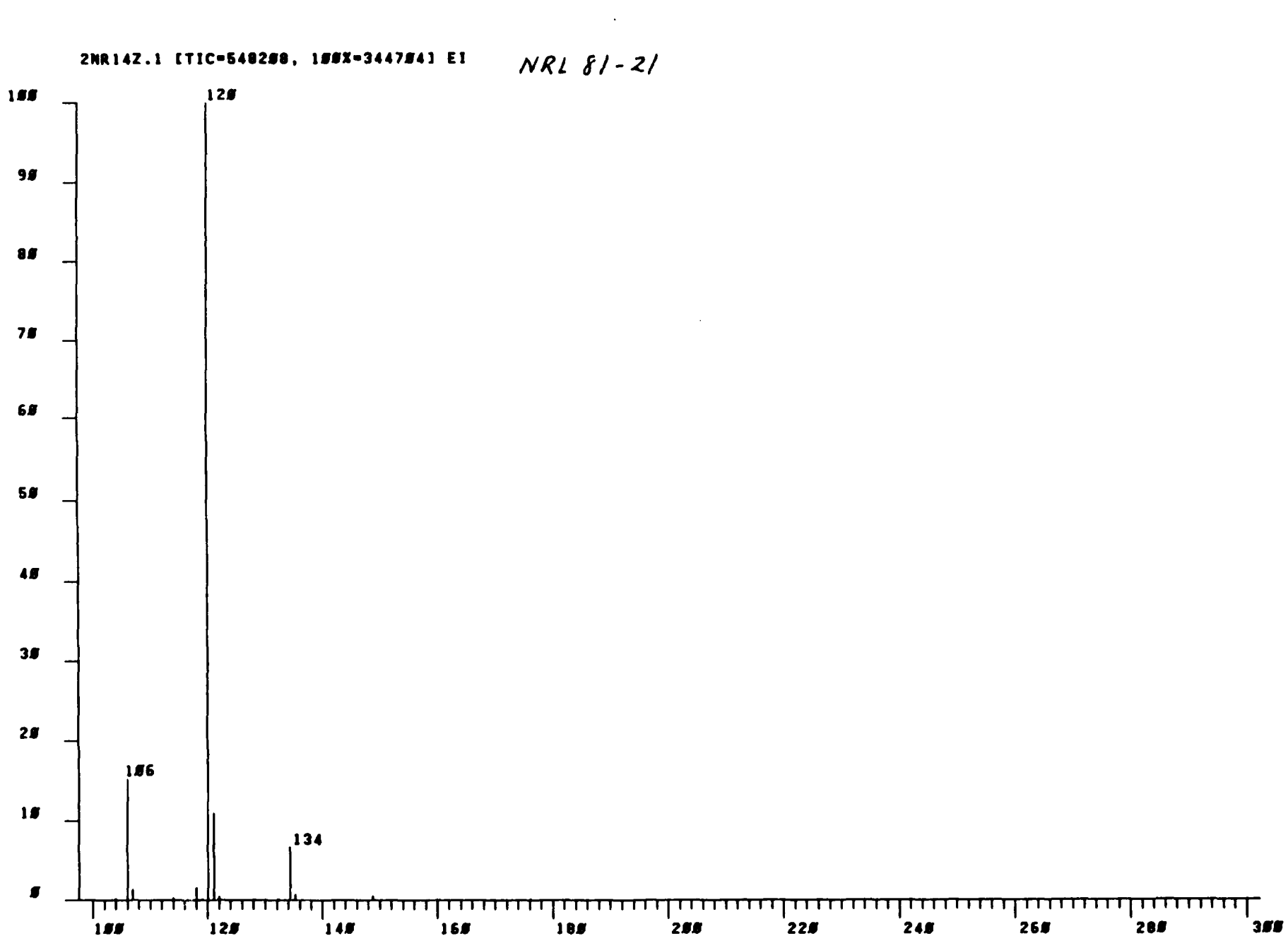
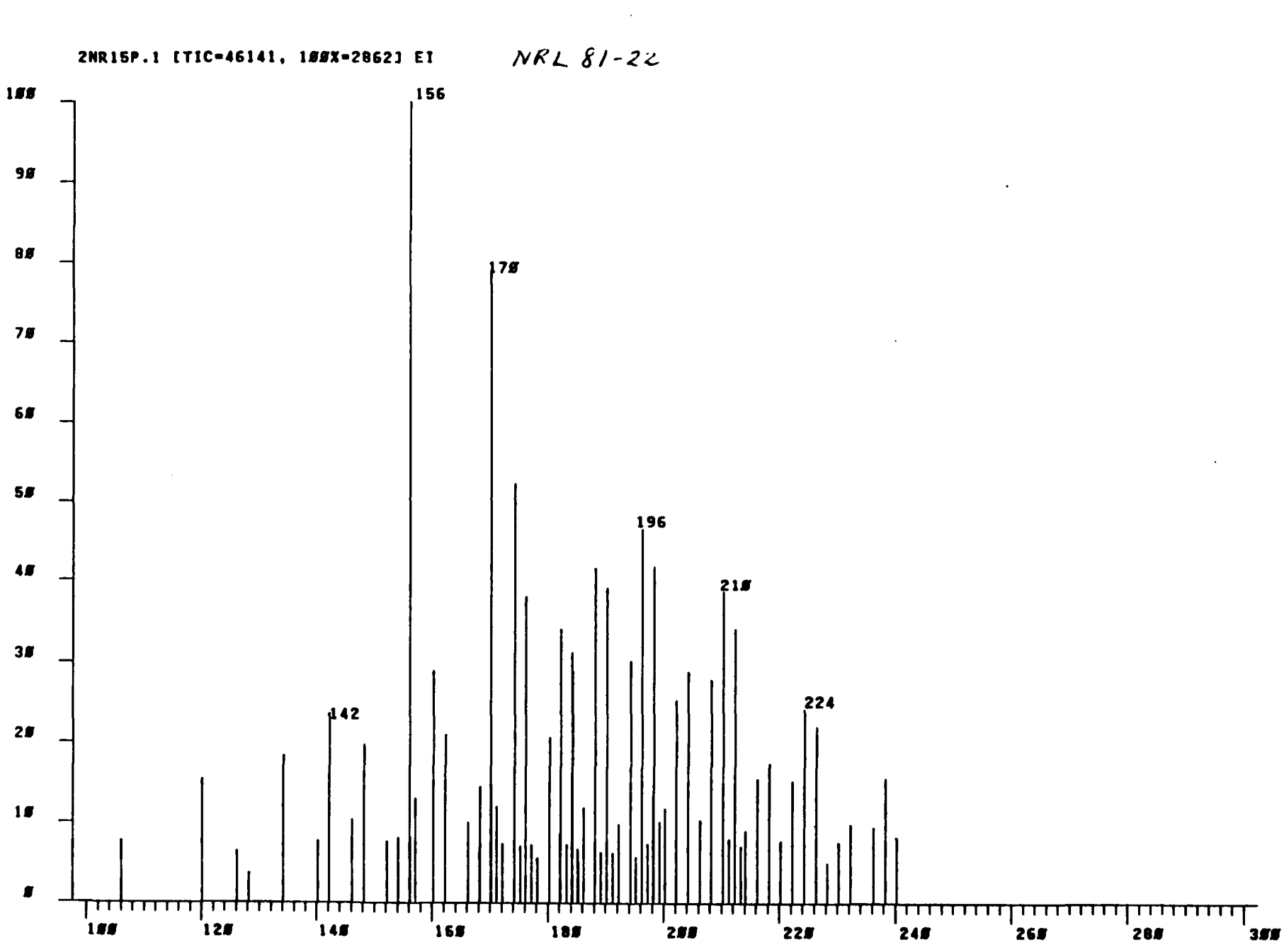
200
220
240
260
280
300


2NR14Z.1 [TIC=548288, 100%=344784] EI
NRL 81-21
100
90
80
70
60
50
40
30
20
10
0
120
106
134
100
120
140
160
180
200
220
240
260
280
300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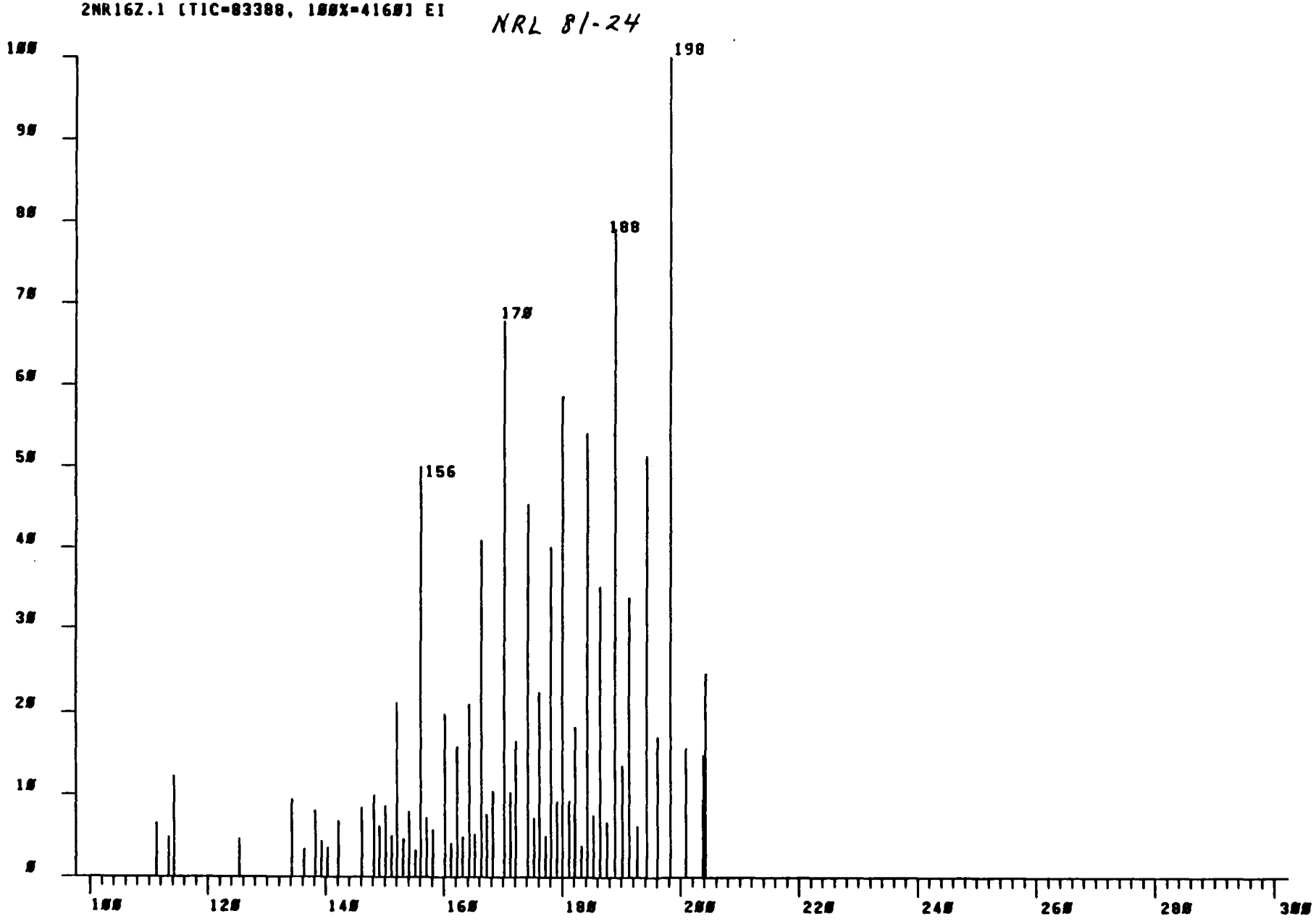
NRL 81-22
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
156
170
196
210
142
224
100%
120%
140%
160%
180%
200%
220%
240%
260%
280%
300%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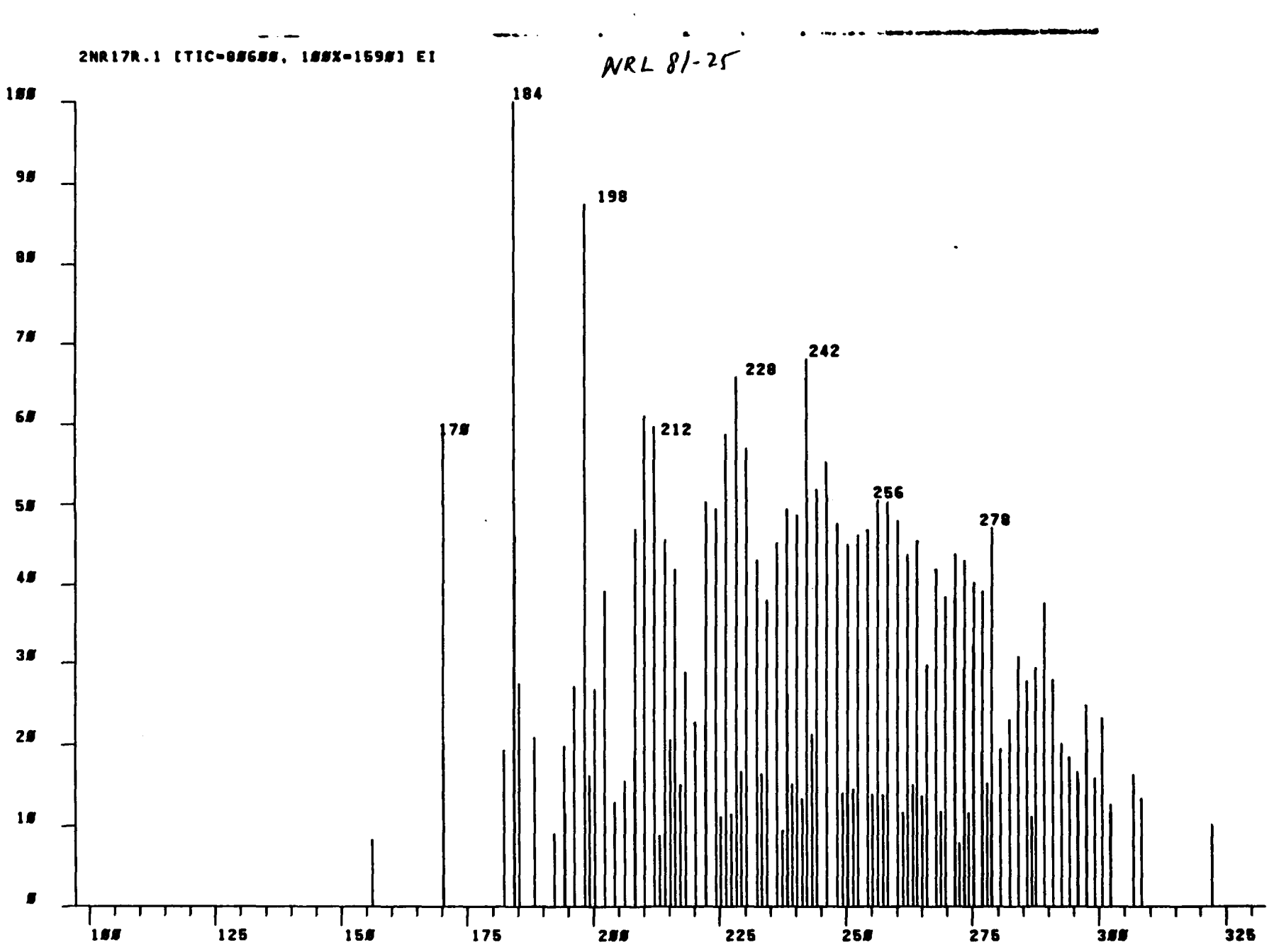
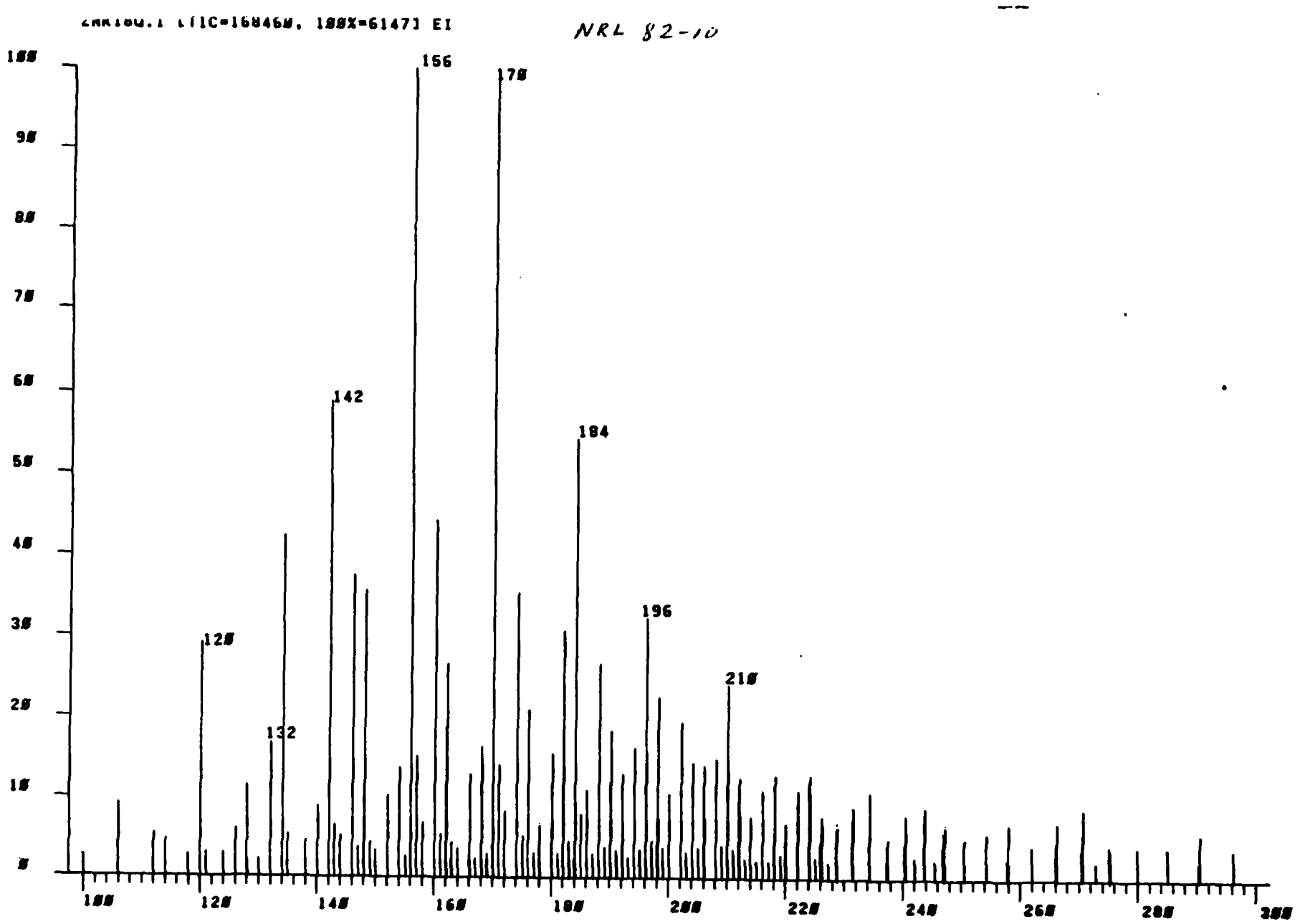
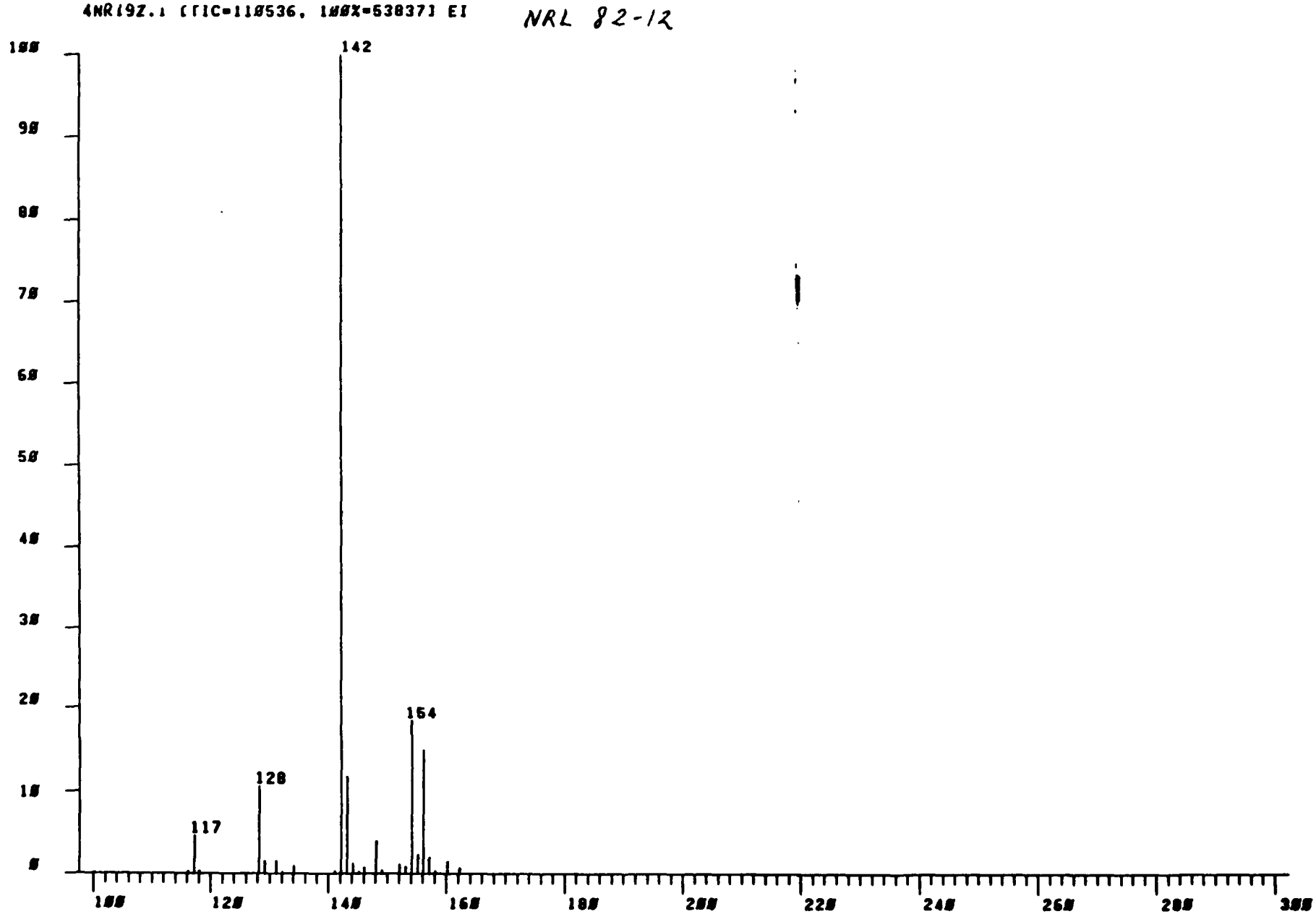
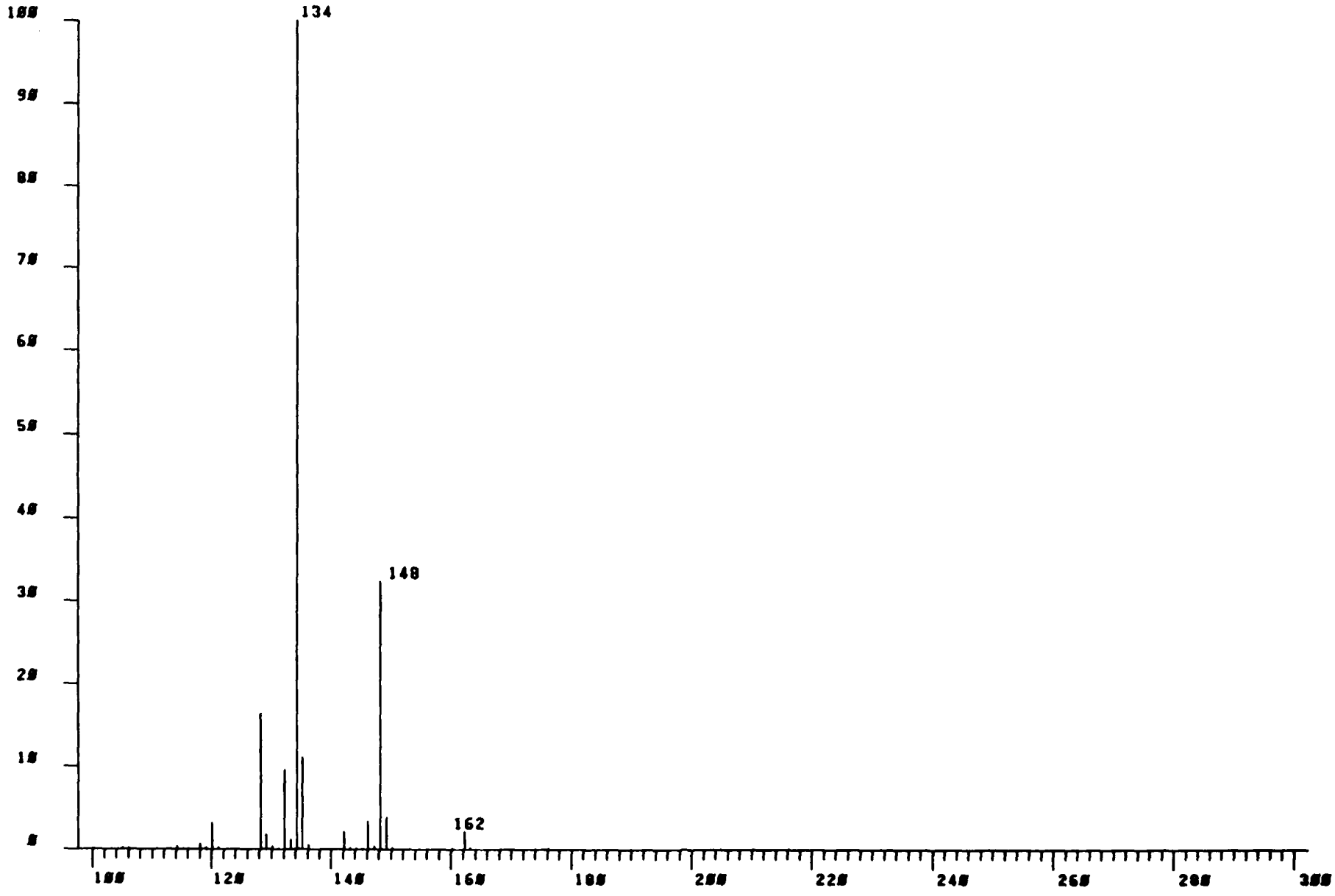
80
70
60
50
40
30
20
10
0
156
170
188
198
100
120
140
160
180
200
220
240
260
280
300


2NR17R.1 [TIC=8#6##, 1##X=159#] EI
NRL 81-25
1##
9#
8#
7#
6#
5#
4#
3#
2#
1#
#
184
198
17#
212
228
242
256
278
1##
125
15#
175
2##
225
25#
275
3##
325

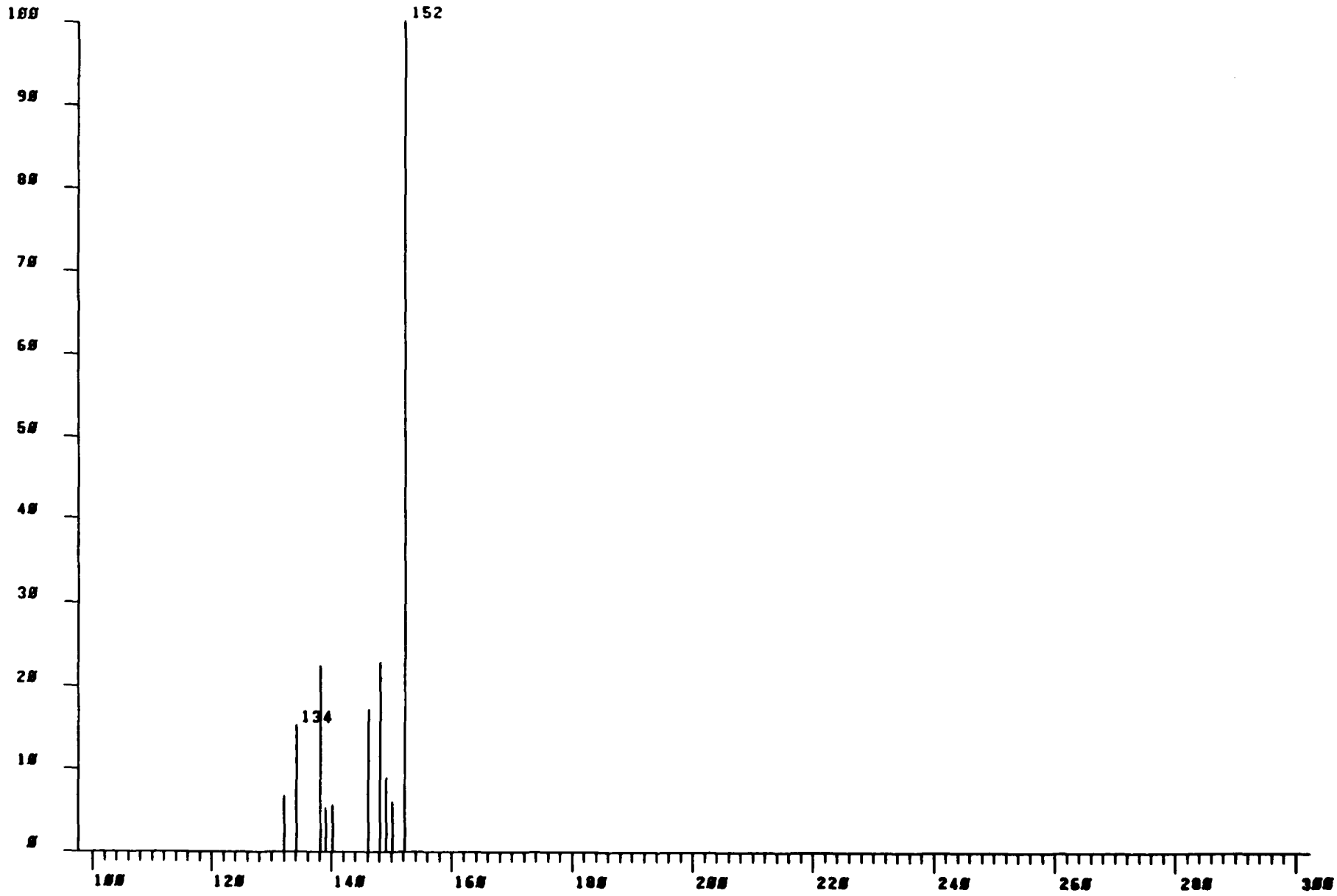

NRL 82-10
156
178
142
184
128
196
132
218
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
100
120
140
160
180
200
220
240
260
280
300

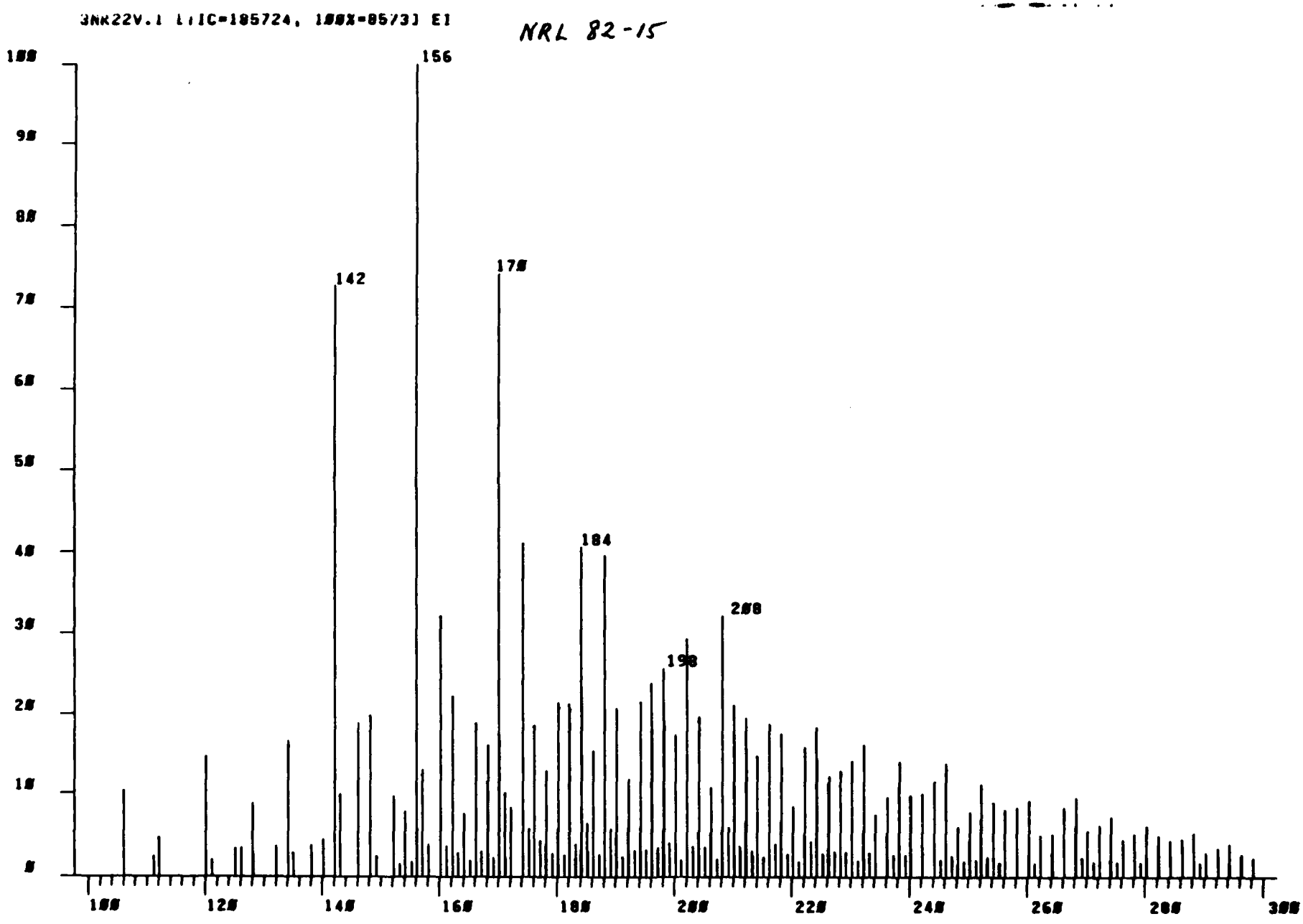

4NR19Z.1 [TIC=110536, 100%=538371] EI
NRL 82-12
100
90
80
70
60
50
40
30
20
10
0
142
154
128
117
100
120
140
160
180
200
220
240
260
280
300

NRL 82-13

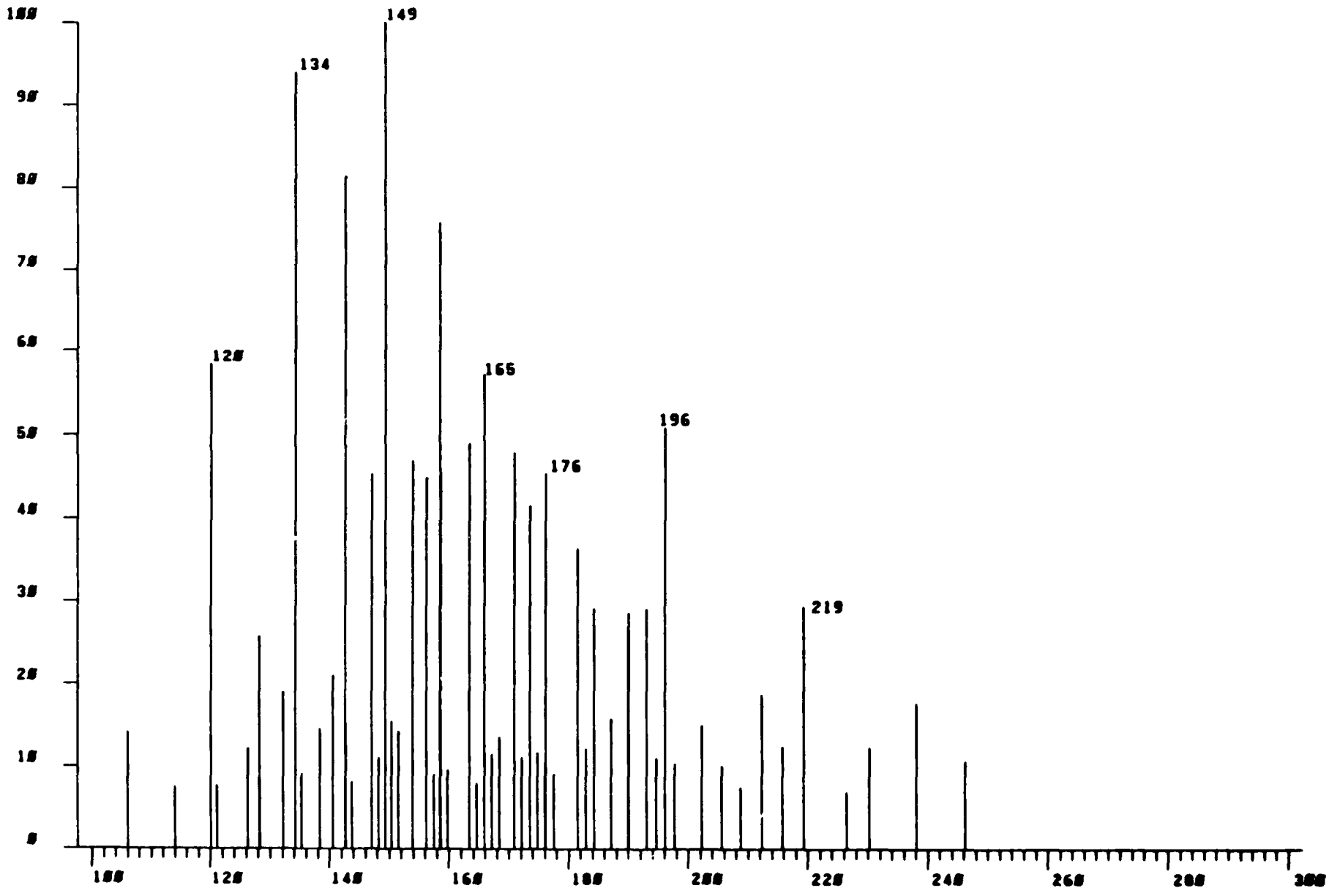

100
90
80
70
60
50
40
30
20
10
0
134
148
162
100
120
140
160
180
200
220
240
260
280
300

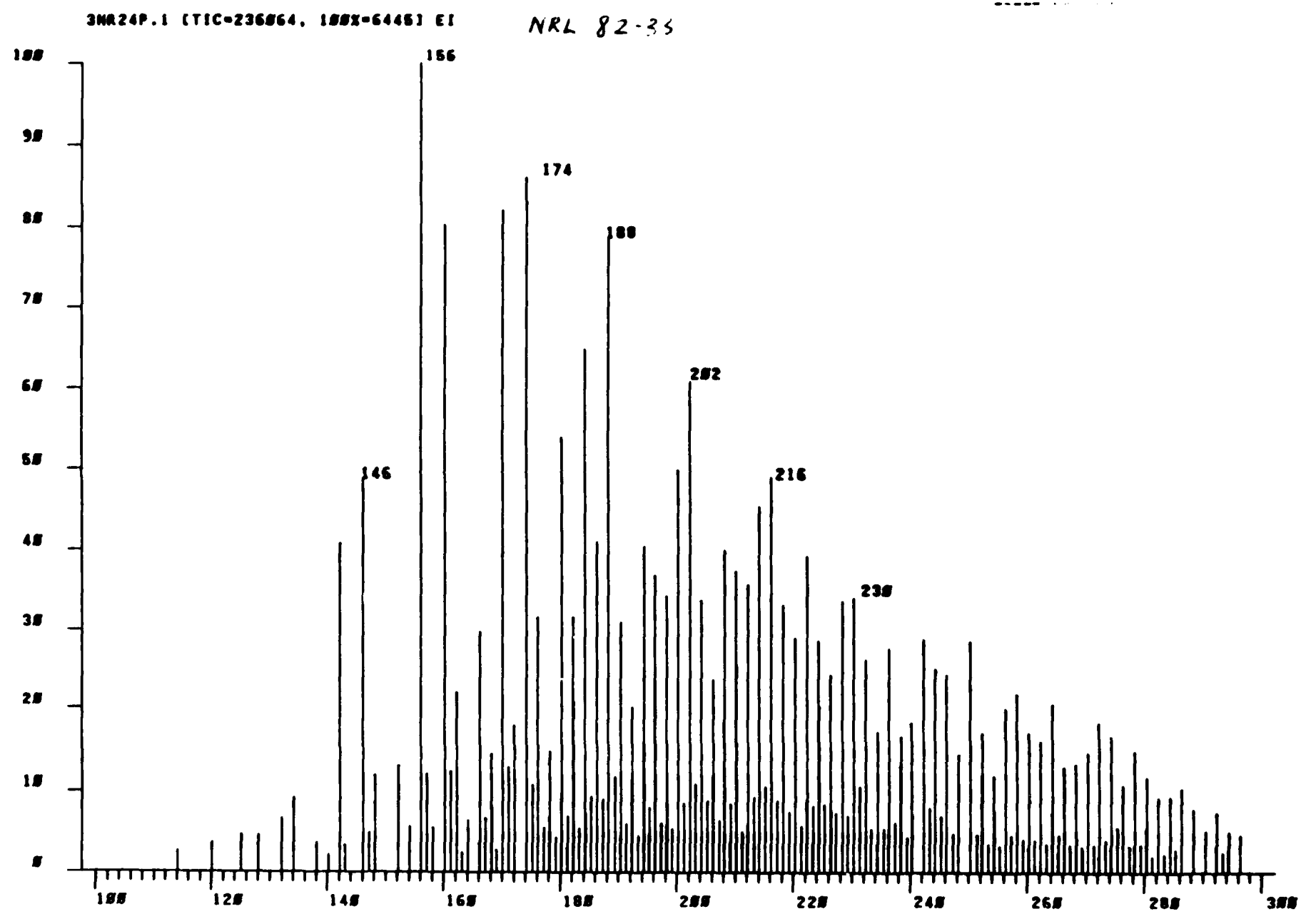
NRL 82-14

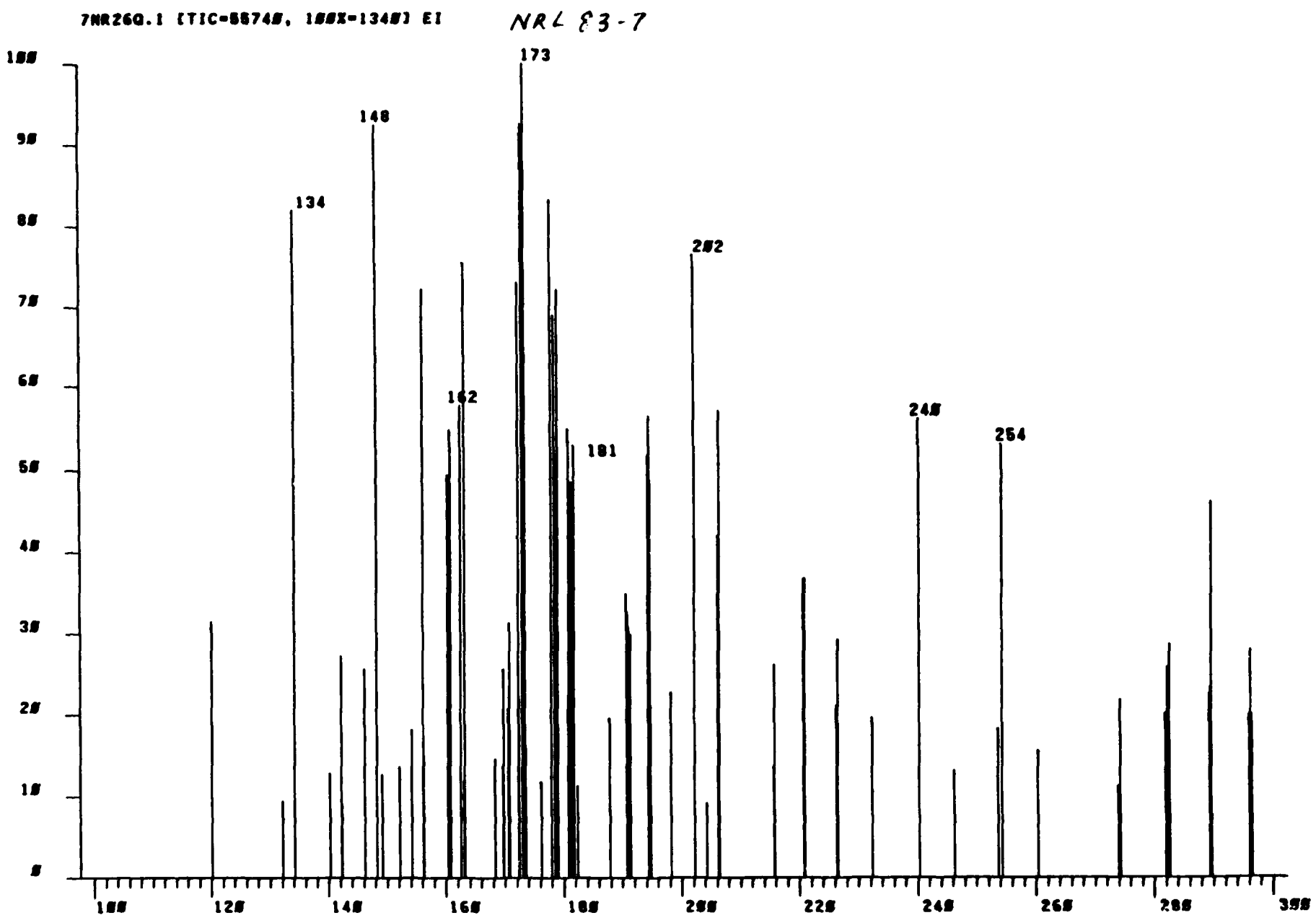

100
90
80
70
60
50
40
30
20
10
0
152
134
100
120
140
160
180
200
220
240
260
280
300


3NK22V.1 [TIC=185724, 100%=85731] EI
NRL 82-15
100
90
80
70
60
50
40
30
20
10
0
156
142
170
184
198
200
100
120
140
160
180
200
220
240
260
280
300

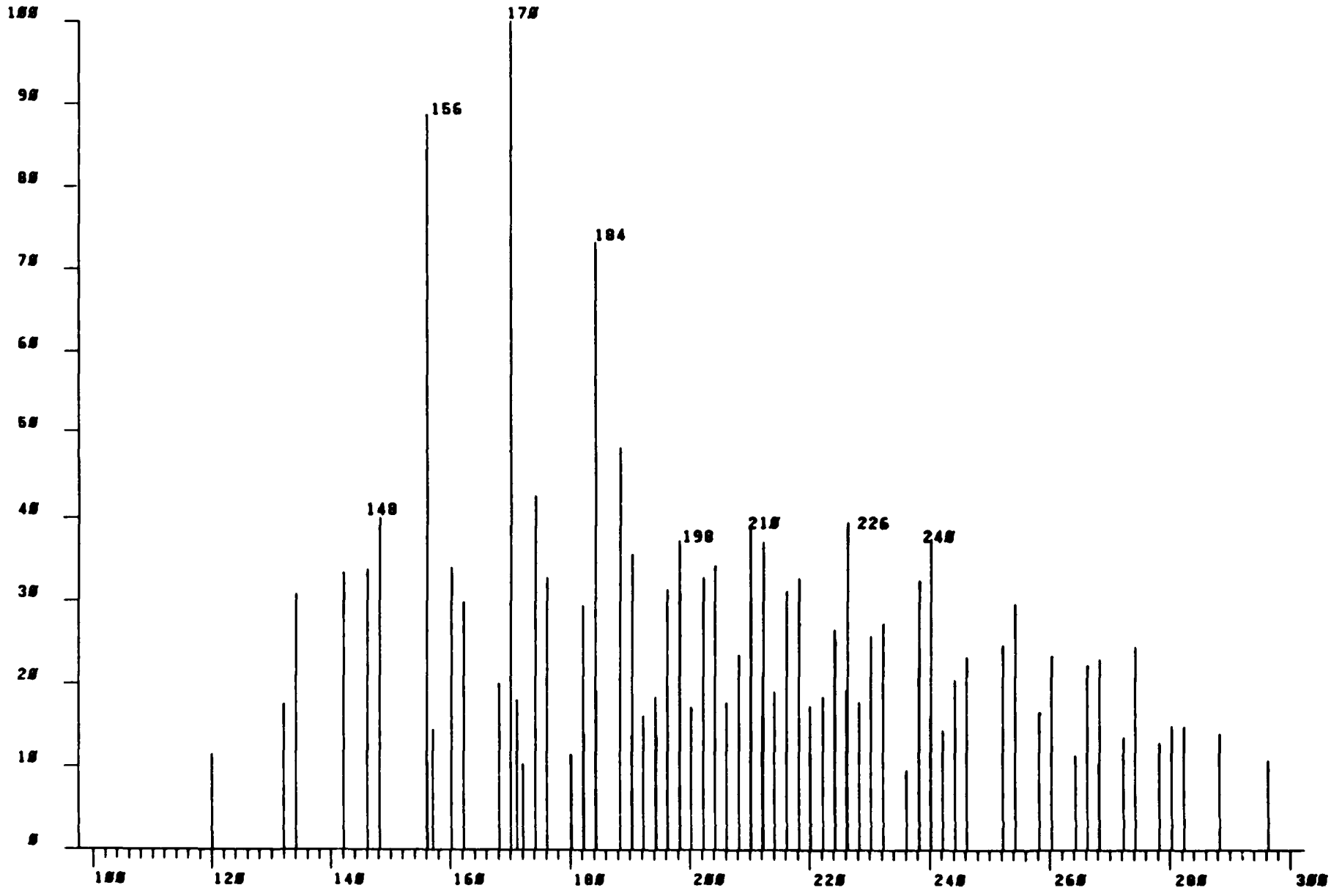
NRL 82-17


100
90
80
70
60
50
40
30
20
10
0
149
134
128
165
196
176
219
100
120
140
160
180
200
220
240
260
280
300


3MR24P.1 [TIC=236864, 100%=64461] EI
NRL 82-35
100
90
80
70
60
50
40
30
20
10
0
156
174
188
202
146
216
230
100
120
140
160
180
200
220
240
260
280
300


7NR26Q.1 [TIC=8674#, 100%=134#] EI
NRL 83-7
100
90
80
70
60
50
40
30
20
10
0
173
148
134
202
162
181
248
264
100
120
140
160
180
200
220
240
260
280
300

NRL 83-14


100
90
80
70
60
50
40
30
20
10
0
156
170
184
148
198
210
226
240
100
120
140
160
180
200
220
240
260
280
300

EDITED VERSION OF DP0:4NR1Z.MS
SCAN: 1, 8/19/86 14:15
IONISATION: FI
NO. PEAKS: 166
BASE/NREF INT: 59978./ 16774.
TIC: 274608.
MASS RANGE: 78.0469 - 400.4069
RETN TIME/MISC: 0: 0/ 0/ 2/ 1

NRL SAMPLE NO. 81-8

SUMMARY OF RESULTS (MOL %)

ACYCLIC SATURATES:	29.2
NAPTHENES:	31.5
MONOAROMATICS:	29.4
POLYAROMATICS:	9.9

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	5.28	1.85	—	—	0.72	—	—	—	—	—	—	—	—	—
9	—	—	—	2.88	—	—	—	—	—	—	—	—	—	—
10	—	4.98	—	—	—	0.39	0.42	—	—	—	—	—	—	—
11	5.40	—	—	1.51	1.12	0.30	—	—	—	—	—	—	—	—
12	4.04	0.57	0.36	2.23	—	0.33	2.19	—	—	0.35	—	—	—	—
13	—	0.95	—	—	2.00	—	—	6.78	—	—	—	—	—	—
14	—	—	0.63	0.45	0.41	2.38	0.42	—	—	—	0.31	—	—	—
15	2.47	2.82	1.27	—	0.40	0.29	1.74	—	—	—	—	0.26	—	—
16	1.47	—	—	2.30	—	—	—	—	0.94	—	—	—	—	—

CONTINUE ...

CONTINUED, NRL 81-8

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
17	1.18	—	—	—	0.93	1.98	0.45	—	—	—	—	—	—	—
18	5.20	0.28	—	—	—	1.01	—	—	—	0.50	—	—	—	—
19	—	—	—	—	0.85	1.65	0.81	—	—	—	—	—	—	—
20	2.65	2.06	0.80	0.96	1.08	1.14	—	—	—	—	—	—	—	—
21	—	—	—	—	1.23	0.79	1.15	0.22	—	—	—	—	—	—
22	—	—	—	0.90	—	0.71	—	—	—	—	0.16	—	—	—
23	—	—	—	1.84	0.83	—	—	—	—	—	—	—	—	—
24	1.49	0.95	—	—	—	0.88	—	—	—	—	—	—	—	—
25	—	—	—	—	0.77	—	—	—	—	—	—	—	—	—
26	—	—	—	—	—	—	—	—	0.42	—	—	—	—	—
27	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	29.17	14.45	3.06	14.02	10.32	11.87	7.18	7.00	1.36	0.85	0.47	0.26	—	—

DPO:3NR2V.MS
SCAN: 1, 4/25/85 10:30

IONISATION: FI
NO. PEAKS: 127
BASE/NREF INT: 18019./ 18019.
TIC: 305360.
MASS RANGE: 57.0703 - 226.2660
RETN TIME/MISC: 0: 0/ 0/ 2/ 0

NRL SAMPLE NO. 81-9A

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 15.0
NAPHTHENES: 42.4
MONOAROMATICS: 34.0
POLYAROMATICS: 8.6

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.20	0.23	0.11	—	0.09	—	—	—	—	—	—	—	—	—
9	0.20	0.42	0.31	—	1.86	0.04	—	—	—	—	—	—	—	—
10	1.39	1.83	1.05	0.12	5.26	1.11	—	0.81	—	—	—	—	—	—
11	3.43	4.18	3.35	0.58	5.94	2.73	0.07	2.81	—	—	—	—	—	—
12	4.03	4.94	4.01	1.43	3.85	2.99	0.14	2.98	0.14	—	—	—	—	—
13	2.89	4.43	3.27	1.56	2.24	2.29	0.40	1.04	0.24	—	—	0.07	—	—
14	2.03	2.84	2.15	1.19	1.30	1.46	0.43	0.28	0.12	—	—	0.04	—	—
15	0.58	1.25	1.28	0.66	0.62	0.56	0.18	0.08	—	—	—	—	—	—
16	0.27	0.52	0.42	0.23	0.26	0.12	0.09	—	—	—	—	—	—	—
SUM	15.02	20.64	15.95	5.77	21.40	11.31	1.31	8.00	0.49	—	—	0.11	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

EDITED VERSION OF DP0:2NR3V.MS
SCAN: 1, 1/31/85 16: 0

IONISATION: FI
NO. PEAKS: 180
BASE/NREF INT: 13633./ 12562.
TIC: 164712.
MASS RANGE: 57.0703 - 324.3756
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-10

SUMMARY OF RESULTS (MOL%)
ACYCLIC SATURATES: 25.9
NAPHTHENES: 19.4
MONOAROMATICS: 23.9
POLYAROMATICS: 30.8

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.46	0.14	—	—	0.44	—	—	—	—	—	—	—	—	—
9	0.33	0.27	—	—	1.22	—	—	—	—	—	—	—	—	—
10	0.60	0.40	0.23	—	1.79	0.34	—	0.37	—	—	—	—	—	—
11	1.78	0.74	0.53	—	1.54	1.37	—	3.04	—	—	—	—	—	—
12	2.25	0.73	0.83	0.20	1.22	2.18	0.14	7.96	0.11	—	—	—	—	—
13	1.30	3.30	0.79	0.27	0.92	1.98	0.33	7.51	0.66	0.08	—	—	—	—
14	4.14	0.42	0.76	0.30	0.71	1.44	0.46	3.27	1.09	0.25	—	0.10	—	—
15	2.37	1.02	1.54	0.41	0.75	0.95	0.51	0.10	1.01	0.36	—	0.45	—	—
16	2.29	0.95	0.96	0.37	0.67	0.67	0.59	0.67	0.80	0.38	0.45	0.08	—	—
17	2.18	0.54	0.37	0.30	0.39	0.44	0.39	0.31	0.51	0.16	0.17	0.06	—	—
18	2.22	0.46	0.30	0.30	0.35	0.36	0.24	0.21	0.18	0.10	—	—	—	—
19	2.30	0.46	0.21	0.24	0.42	0.22	0.19	0.12	0.09	—	—	—	—	—

CONTINUE ...

CONTINUED, NRL 81-10

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
20	1.85	0.27	0.19	0.17	0.15	0.16	0.12	0.09	0.06	—	—	—	—	—
21	0.91	0.23	0.15	—	0.11	0.09	0.08	—	—	—	—	—	—	—
22	0.55	—	—	—	—	—	—	—	—	—	—	—	—	—
23	0.33	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	25.87	9.95	6.87	2.55	10.68	10.21	3.04	23.66	4.51	1.34	0.62	0.69	—	—

DPO:3NR4V.MS
SCAN: 1, 1/31/85 10:26

IONISATION: FI
NO. PEAKS: 101
BASE/NREF INT: 3693./ 2934.
TIC: 56543.
MASS RANGE: 57.0703 - 268.3130
RETN TIME/MISC: 0: 0/ 0/ 1/ 0

NRL SAMPLE NO. 81-11

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 22.5
NAPHTHENES: 25.5
MONOAROMATICS: 29.8
POLYAROMATICS: 22.2

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	—	—	—	—	0.41	—	—	—	—	—	—	—	—	—
9	—	0.36	—	—	1.28	—	—	—	—	—	—	—	—	—
10	0.89	0.76	—	—	2.15	0.59	—	0.50	—	—	—	—	—	—
11	1.82	1.11	0.91	—	2.35	1.76	—	3.09	—	—	—	—	—	—
12	2.40	1.27	1.43	0.40	1.57	2.70	—	6.01	0.22	—	—	—	—	—
13	3.16	1.67	1.33	0.69	1.38	2.57	0.37	4.78	0.39	—	—	0.18	—	—
14	3.62	1.70	1.48	0.65	1.25	2.26	0.48	2.31	0.68	—	0.18	0.20	—	—
15	3.33	1.46	2.47	0.77	1.08	1.28	0.62	0.84	0.65	0.18	0.24	—	—	—
16	2.99	1.22	1.12	0.68	0.88	0.87	0.57	0.42	0.42	0.16	0.23	—	—	—
17	1.91	0.77	0.57	0.51	0.56	0.51	0.41	0.26	0.25	—	—	—	—	—
18	1.35	0.71	0.48	0.39	0.54	0.43	0.23	—	—	—	—	—	—	—
19	1.07	0.58	—	—	0.35	0.33	—	—	—	—	—	—	—	—
SUM	22.52	11.60	9.80	4.09	13.79	13.32	2.68	18.22	2.61	0.35	0.64	0.38	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DPO:2NR5V.MS
SCAN: 1, 9/21/84 10:30

IONISATION: EI
NO. PEAKS: 72
BASE/NREF INT: 11485./ 2321.
TIC: 78744.
MASS RANGE: 57.0703 - 254.2973
RETN TIME/MISC: 0: 0/ 0/ 3/ 0

NRL SAMPLE NO. 81-12

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 30.0
NAPHTHENES: 33.8
MONOAROMATICS: 23.7
POLYAROMATICS: 12.6

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	1.39	—	—	—	0.48	—	—	—	—	—	—	—	—	—
9	—	0.55	—	—	1.54	—	—	—	—	—	—	—	—	—
10	1.88	1.53	0.64	—	3.13	0.55	—	0.65	—	—	—	—	—	—
11	4.30	3.37	1.91	—	3.15	1.53	—	2.35	—	—	—	—	—	—
12	5.15	4.31	2.35	0.82	2.47	1.92	—	3.93	—	—	—	—	—	—
13	5.04	3.58	2.06	0.93	1.47	1.93	—	3.07	0.28	—	—	—	—	—
14	4.39	2.37	1.67	0.87	0.84	1.25	0.37	1.14	0.30	—	—	—	—	—
15	3.18	1.49	1.82	0.62	0.72	0.79	0.35	0.54	0.30	—	—	—	—	—
16	2.08	1.02	0.72	0.41	0.43	0.41	0.40	—	—	—	—	—	—	—
17	1.38	0.73	—	—	—	—	—	—	—	—	—	—	—	—
18	1.17	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	29.95	18.96	11.16	3.65	14.22	8.38	1.11	11.68	0.88	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DPO:2NR6V.MS
SCAN: 1, 4/25/85 11:19

IONISATION: FI
NO. PEAKS: 123
BASE/NREF INT: 41858./ 7248.
TIC: 176156.
MASS RANGE: 57.0703 - 246.2347
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-13

SUMMARY OF RESULTS (MOL %)

ACYCLIC SATURATES:	16.1
NAPHTHENES:	20.8
MONOAROMATICS:	50.6
POLYAROMATICS:	12.5

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.35	0.20	—	—	4.42	—	—	—	—	—	—	—	—	—
9	0.27	0.19	—	0.22	24.02	0.29	—	—	—	—	—	—	—	—
10	0.49	0.39	0.19	—	3.15	0.31	—	0.12	—	—	—	—	—	—
11	1.05	0.97	0.43	—	1.43	0.85	—	1.01	—	—	—	—	—	—
12	1.50	1.22	0.94	0.13	1.24	1.49	0.10	4.35	0.07	—	—	—	—	—
13	2.97	1.97	1.25	0.37	1.68	2.10	0.22	3.84	0.14	—	—	—	—	—
14	3.52	2.38	1.38	0.69	1.54	1.88	0.44	1.49	0.28	0.06	—	—	—	—
15	3.05	2.05	1.44	0.51	1.18	1.32	0.42	0.42	0.17	—	—	—	—	—
16	2.17	1.41	0.94	0.38	0.70	0.75	0.30	0.16	0.09	—	—	—	—	—
17	0.69	0.61	0.37	0.19	0.28	0.23	0.16	0.08	0.07	—	—	—	—	—
18	—	—	—	—	0.11	—	—	0.09	0.06	—	—	—	—	—
SUM	16.07	11.39	6.95	2.47	39.75	9.22	1.65	11.56	0.88	0.06	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DPO:1NR7V.MS
SCAN: 1, 4/25/85 11:24

IONISATION: FI
NO. PEAKS: 114
BASE/NREF INT: 11231./ 9988.
TIC: 134256.
MASS RANGE: 57.0703 - 246.2347
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-14

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 17.5
NAPHTHENES: 26.4
MONOAROMATICS: 33.1
POLYAROMATICS: 23.0

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.30	—	—	—	1.90	—	—	—	—	—	—	—	—	—
9	0.28	0.31	—	—	5.12	—	—	—	—	—	—	—	—	—
10	0.35	0.27	—	—	0.90	0.14	—	0.22	—	—	—	—	—	—
11	0.41	0.37	0.34	—	0.74	0.36	—	2.06	—	—	—	—	—	—
12	0.91	0.65	0.47	0.21	0.81	1.21	0.16	7.82	0.11	—	—	—	—	—
13	1.89	1.27	1.41	0.56	1.25	2.57	0.55	6.93	0.62	0.09	—	—	—	—
14	4.47	3.05	2.13	0.97	2.42	3.33	1.30	2.71	0.68	0.12	—	0.11	—	—
15	4.66	4.01	3.11	1.05	2.35	2.55	1.12	0.79	0.30	—	—	0.09	—	—
16	3.40	2.41	1.43	0.94	1.24	1.12	0.59	0.20	—	—	—	—	—	—
17	0.80	0.73	0.46	0.26	0.38	0.39	0.25	0.09	0.08	—	—	—	—	—
18	—	—	—	—	0.15	0.18	—	—	—	—	—	—	—	—
SUM	17.49	13.08	9.34	3.99	17.24	11.86	3.97	20.81	1.79	0.22	—	0.21	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DP0:2NR8V.MS
SCAN: 1, 9/21/84 10:17

IONISATION: FI
NO. PEAKS: 81
BASE/NREF INT: 10072./ 3343.
TIC: 102260.
MASS RANGE: 57.0703 - 240.2817
RETN TIME/MISC: 0: 0/ 0/ 1/ 0

NRL SAMPLE NO. 81-15

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 29.4
NAPHTHENES: 29.8
MONOAROMATICS: 34.1
POLYAROMATICS: 6.7

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.75	—	—	—	6.12	—	—	—	—	—	—	—	—	—
9	—	—	—	—	7.57	—	—	—	—	—	—	—	—	—
10	1.11	1.05	0.53	—	3.30	0.71	—	0.24	—	—	—	—	—	—
11	5.35	3.46	2.01	—	3.13	2.13	—	0.93	—	—	—	—	—	—
12	6.32	3.44	2.38	0.42	2.03	1.90	—	2.52	—	—	—	—	—	—
13	5.15	3.48	2.17	0.54	1.53	1.24	—	2.05	0.12	—	—	—	—	—
14	4.29	2.86	1.16	0.48	0.92	0.99	0.24	0.63	—	—	—	—	—	—
15	3.57	1.64	1.36	0.36	0.54	0.63	0.28	0.21	—	—	—	—	—	—
16	1.90	1.02	0.44	0.37	0.28	0.35	—	—	—	—	—	—	—	—
17	1.00	0.61	—	—	0.19	—	—	—	—	—	—	—	—	—
SUM	29.44	17.56	10.05	2.17	25.62	7.94	0.51	6.58	0.12	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DPO:2NR9V.MS
SCAN: 1, 9/21/84 10:54

IONISATION: FI
NO. PEAKS: 94
BASE/NREF INT: 16051./ 3737.
TIC: 122968.
MASS RANGE: 57.0703 - 240.2817
RETN TIME/MISC: 0: 0/ 0/ 1/ 0

NRL SAMPLE NO. 81-16

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 32.7
NAPHTHENES: 35.2
MONOAROMATICS: 26.4
POLYAROMATICS: 5.7

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	1.14	0.28	—	—	0.90	—	—	—	—	—	—	—	—	—
9	—	0.40	—	—	5.20	—	—	—	—	—	—	—	—	—
10	1.17	1.10	0.85	—	3.20	0.78	—	0.21	—	—	—	—	—	—
11	6.57	3.90	2.48	—	3.32	2.08	—	0.76	—	—	—	—	—	—
12	6.85	4.07	2.63	0.55	2.16	1.61	—	2.01	—	—	—	—	—	—
13	6.63	3.59	2.32	0.69	1.35	1.27	0.20	1.80	—	—	—	—	—	—
14	4.74	3.09	1.76	0.61	0.77	0.98	0.28	0.66	—	—	—	—	—	—
15	2.71	1.76	1.13	0.46	0.60	0.58	0.19	0.22	—	—	—	—	—	—
16	2.18	1.56	0.75	0.33	0.33	0.32	—	—	—	—	—	—	—	—
17	0.72	0.57	0.34	—	0.28	—	—	—	—	—	—	—	—	—
SUM	32.70	20.32	12.25	2.64	18.13	7.62	0.68	5.65	—	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DPO:2NR10W.MS
SCAN: 1, 4/22/85 15:39

IONISATION: FI
NO. PEAKS: 131
BASE/NREF INT: 11537./ 11537.
TIC: 167136.
MASS RANGE: 57.0703 - 240.2817
RETN TIME/MISC: 0: 0/ 0/ 1/ 0

NRL SAMPLE NO. 81-17

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 11.2
NAPHTHENES: 26.3
MONOAROMATICS: 44.0
POLYAROMATICS: 18.5

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.30	0.14	0.16	—	0.11	—	—	—	—	—	—	—	—	—
9	—	0.33	0.11	—	1.01	0.23	—	—	—	—	—	—	—	—
10	0.63	1.36	1.32	—	2.56	5.90	—	0.38	—	—	—	—	—	—
11	2.60	4.13	3.93	0.33	4.57	9.80	0.12	2.41	—	—	—	—	—	—
12	3.04	4.37	3.36	0.58	4.89	7.70	0.27	6.31	0.09	—	—	—	—	—
13	—	3.01	—	—	2.18	3.50	0.44	5.83	0.80	0.09	—	—	—	—
14	2.59	0.28	—	—	—	—	—	—	—	—	—	—	—	—
15	1.11	1.20	0.62	0.23	0.53	—	—	0.08	—	—	—	—	—	—
16	0.60	0.40	0.29	—	0.16	—	0.05	0.28	0.49	0.33	0.48	—	—	—
17	0.35	—	0.11	—	—	—	—	—	0.23	0.14	0.23	0.06	—	—
18	—	—	—	—	—	—	—	—	0.08	—	—	—	—	—
SUM	11.23	15.22	9.89	1.15	16.01	27.13	0.88	15.31	1.69	0.57	0.71	0.06	—	—

EDITED VERSION OF DP0:2NR11P.MS
SCAN: 1, 2/18/87 14:41

IONISATION: FI
NO. PEAKS: 88
BASE/NREF INT: 6104./ 6104.
TIC: 75300.
MASS RANGE: 78.0469 - 212.1565
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-18

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 8.8
NAPHTHENES: 25.6
MONOAROMATICS: 41.6
POLYAROMATICS: 24.0

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	—	—	—	—	0.68	0.26	—	—	—	—	—	—	—	—
10	0.66	1.18	0.96	—	2.34	4.95	—	0.34	—	—	—	—	—	—
11	2.19	3.60	3.00	—	4.01	9.44	—	2.36	—	—	—	—	—	—
12	2.41	4.22	2.79	0.53	4.05	6.75	0.26	6.99	—	—	—	—	—	—
13	2.21	2.69	1.50	0.74	2.13	3.15	0.33	5.46	0.80	0.09	—	—	—	—
14	1.29	1.29	0.90	0.54	0.95	1.29	0.33	2.42	1.10	0.25	0.16	—	—	—
15	—	0.59	0.71	0.38	0.43	—	0.22	0.90	0.93	0.38	0.39	—	—	—
16	—	—	—	—	—	—	—	0.31	0.38	0.27	0.52	—	—	—
17	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	8.76	13.57	9.86	2.19	14.60	25.84	1.14	18.79	3.20	0.99	1.07	—	—	—

DPO:4NR12V.MS
SCAN: 1, 4/ 8/85 11:24

IONISATION: FI
NO. PEAKS: 93
BASE/NREF INT: 17407./ 17407.
TIC: 180140.
MASS RANGE: 57.0703 - 212.1565
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-19A

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 10.0
NAPHTHENES: 31.0
MONOAROMATICS: 33.5
POLYAROMATICS: 25.5

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	—	0.25	0.48	—	—	—	—	—	—	—	—	—	—	—
9	—	1.04	0.66	—	0.99	0.54	—	11.64	—	—	—	—	—	—
10	—	—	—	0.17	3.25	9.94	—	0.31	—	—	0.07	—	—	—
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12	4.55	6.80	5.65	1.11	7.17	0.99	—	0.97	2.57	3.09	0.27	4.21	1.09	—
13	3.57	4.53	3.22	1.53	3.64	3.26	0.31	0.20	0.15	—	—	—	—	—
14	1.91	2.52	1.65	1.04	1.37	1.21	0.18	—	0.11	—	—	—	—	—
15	—	—	—	0.30	0.42	0.26	—	—	—	—	—	—	—	—
16	—	—	—	—	—	—	—	0.37	—	—	—	—	—	—
SUM	10.03	15.14	11.67	4.15	16.84	16.20	0.49	13.49	2.83	3.09	0.34	4.21	1.09	—

EDITED VERSION OF DP0:2NR13P.MS
SCAN: 1, 8/29/86 18: 0

IONISATION: FI
NO. PEAKS: 55
BASE/NREF INT: 5089./ 5089.
TIC: 65964.
MASS RANGE: 57.0703 - 338.3912
RETN TIME/MISC: 0: 0/ 0/ 7/ 0

NRL SAMPLE NO. 81-20

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 39.8
NAAPHTHENES: 32.8
MONOAROMATICS: 26.6
POLYAROMATICS: 0.8

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
7	—	—	—	—	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	0.80	—	—	—	—	—	—	—	—	—
9	7.91	—	—	—	4.20	—	—	—	—	—	—	—	—	—
10	—	—	9.68	—	—	—	—	—	—	—	—	—	—	—
11	2.10	—	—	—	4.12	—	—	—	—	0.35	—	—	—	—
12	—	5.03	—	—	0.85	—	—	—	—	—	—	—	—	—
13	6.58	—	—	—	2.95	—	—	—	—	—	—	—	—	—
14	—	—	8.61	—	—	—	—	—	—	—	—	—	—	—
15	9.84	—	—	—	2.55	—	—	—	—	0.48	—	—	—	—
16	—	—	—	—	—	—	—	—	—	—	—	—	—	—

CONTINUE ...

CONTINUED, NRL 81-20

CARB# \ TRUE Z ->

17	—	3.01	—	—	1.96	—	—	—	—	—	—	—	—	—
18	—	4.74	—	—	1.66	—	—	—	—	—	—	—	—	—
19	—	1.69	—	—	0.54	—	—	—	—	—	—	—	—	—
20	5.77	—	—	—	2.49	—	—	—	—	—	—	—	—	—
21	—	—	—	—	—	—	—	—	—	—	—	—	—	—
22	—	—	—	—	2.92	—	—	—	—	—	—	—	—	—
23	—	—	—	—	1.57	—	—	—	—	—	—	—	—	—
24	7.59	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	39.79	14.47	18.29	—	26.62	—	—	—	—	0.83	—	—	—	—

DP0:2NR14M.MS
SCAN: 1, 5/13/87 16:13

IONISATION: FI
NO. PEAKS: 44
BASE/NREF INT: 301040./ 31307.
TIC: 490544.
MASS RANGE: 57.0703 - 148.1252
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 81-21

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 0.5
NAAPHTHENES: 0.7
MONOAROMATICS: 98.7
POLYAROMATICS: 0.1

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
7	0.09	—	—	—	—	—	—	—	—	—	—	—	—	—
8	0.39	0.04	—	0.08	12.73	0.17	—	—	—	—	—	—	—	—
9	—	—	—	0.59	78.38	1.33	0.03	—	—	—	—	—	—	—
10	—	—	—	—	5.42	0.22	—	0.06	—	—	—	—	—	—
11	—	—	—	—	0.39	0.04	—	0.03	—	—	—	—	—	—
SUM	0.49	0.04	—	0.67	96.93	1.76	0.03	0.08	—	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

DP0:2NR15P.MS
SCAN: 1, 2/19/87 11:46

IONISATION: FI
NO. PEAKS: 79
BASE/NREF INT: 3229./ 2263.
TIC: 46141.
MASS RANGE: 57.0703 - 240.2817
RETN TIME/MISC: 0: 0/ 0/ 3/ 0

NRL SAMPLE NO. 81-22

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 27.5
NAPHTHENES: 32.7
MONOAROMATICS: 25.6
POLYAROMATICS: 14.1

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	—	—	—	—	0.42	—	—	—	—	—	—	—	—	—
9	0.54	0.59	—	—	0.84	—	—	—	—	—	—	—	—	—
10	0.94	0.71	—	—	0.99	—	—	—	—	—	—	—	—	—
11	1.20	0.74	0.60	—	1.07	0.59	—	1.12	—	—	—	—	—	—
12	2.13	1.32	0.78	—	1.13	1.65	—	5.40	—	—	—	—	—	—
13	4.93	3.75	1.61	0.50	2.43	3.39	0.35	4.35	0.23	—	—	—	—	—
14	7.49	4.92	2.81	0.87	2.44	2.73	0.57	1.81	0.29	—	—	—	—	—
15	5.94	4.23	2.17	0.91	1.55	1.45	0.56	0.65	0.26	—	—	—	—	—
16	3.19	2.19	1.19	0.68	0.94	0.88	0.43	—	—	—	—	—	—	—
17	1.19	1.41	0.74	—	0.53	0.43	0.24	—	—	—	—	—	—	—
SUM	27.54	19.86	9.90	2.95	12.33	11.14	2.16	13.32	0.79	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

EDITED VERSION OF DP0:2NR16Z.MS
SCAN: 1, 8/29/86 12:59

IONISATION: FI
NO. PEAKS: 75
BASE/NREF INT: 13764./ 3286.
TIC: 83388.
MASS RANGE: 57.0704 - 204.1878
RETN TIME/MISC: 0: 0/ 0/ 1/ 0

NRL SAMPLE NO. 81-24

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 63.2
NAPHTHENES: 4.7
MONOAROMATICS: 21.3
POLYAROMATICS: 10.8

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	—	—	0.36	—	1.58	—	—	—	—	—	—	—	—	—
10	9.03	0.86	0.87	0.42	0.70	—	—	—	—	—	—	—	—	—
11	9.96	—	—	1.06	0.74	0.67	—	—	0.17	—	—	—	—	—
12	13.52	0.60	—	—	1.18	0.33	0.38	—	0.37	0.22	0.37	—	—	—
13	10.79	0.48	—	—	1.68	0.57	1.09	—	0.49	2.76	0.99	—	—	—
14	19.92	—	—	—	1.01	6.22	2.31	—	0.86	—	1.88	—	—	—
15	—	—	—	—	1.84	—	1.03	—	—	2.41	0.29	—	—	—
16	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SUM	63.21	1.94	1.23	1.48	8.74	7.79	4.81	—	1.89	5.38	3.53	—	—	—

EDITED VERSION OF DP0:2NR17R.MS
SCAN: 1, 5/ 8/87 18:11

IONISATION: FI
NO. PEAKS: 124
BASE/NREF INT: 9865./ 1590.
TIC: 80600.
MASS RANGE: 57.0703 - 322.3599
RETN TIME/MISC: 0: 0/ 0/ 7/ 0

NRL SAMPLE NO. 81-25

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 29.6
NAPHTHENES: 36.1
MONOAROMATICS: 20.7
POLYAROMATICS: 13.6

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
12	1.50	—	—	—	—	—	—	0.21	—	—	—	—	—	—
13	—	0.91	1.85	—	—	—	—	1.46	—	—	—	—	—	—
14	7.70	1.26	0.47	0.41	—	0.61	—	2.45	—	—	—	—	—	—
15	4.44	2.85	1.88	0.70	0.36	1.15	0.65	2.14	—	0.35	—	—	—	—
16	5.22	0.52	2.02	1.02	0.80	1.67	1.12	1.47	—	0.32	—	—	—	—
17	3.62	0.55	1.81	1.72	1.20	1.67	1.61	—	0.87	0.39	0.29	—	—	—
18	4.51	2.05	1.80	2.15	1.53	1.53	1.67	—	0.87	—	—	—	—	—
19	0.89	1.39	1.82	1.97	1.33	1.48	—	—	0.81	0.27	—	—	—	—
20	1.71	0.91	0.53	0.87	0.33	0.23	—	—	—	—	0.26	—	—	—
21	—	0.87	0.81	1.25	0.81	0.33	—	—	—	0.83	—	0.57	—	—
22	—	0.63	0.66	—	0.35	0.27	—	—	—	—	—	—	—	—
23	—	0.48	—	—	—	—	—	—	—	—	—	—	—	—
SUM	29.58	12.41	13.64	10.09	6.71	8.95	5.06	7.73	2.54	2.16	0.56	0.57	—	—

EDITED VERSION OF DP0:2NR18Q.MS
SCAN: 1, 2/24/87 17:23

IONISATION: FI
NO. PEAKS: 203
BASE/NREF INT: 19081./ 2723.
TIC: 168460.
MASS RANGE: 57.0703 - 338.2972
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 82-10

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 13.5
NAPHTHENES: 29.6
MONOAROMATICS: 26.4
POLYAROMATICS: 30.4

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
7	0.43	—	—	—	—	—	—	—	—	—	—	—	—	—
8	0.76	0.55	—	—	0.55	—	—	—	—	—	-	—	—	—
9	0.33	0.61	0.27	—	1.91	0.18	—	—	—	—	—	—	—	—
10	0.66	0.89	0.39	—	2.82	1.05	0.12	0.60	—	—	—	—	—	—
11	0.89	1.65	0.89	0.34	2.37	2.58	0.28	3.42	—	—	—	—	—	—
12	1.00	1.71	1.31	0.37	1.84	3.12	0.35	6.01	0.16	—	—	0.37	—	—
13	1.54	2.29	1.60	0.43	1.42	2.54	0.44	5.89	0.70	0.11	0.13	0.79	—	—
14	4.21	3.70	1.18	1.52	—	—	—	3.26	1.32	0.24	0.25	0.82	—	—
15	1.31	1.65	1.52	1.36	0.40	1.21	—	0.40	—	—	—	—	—	—
16	1.10	1.09	0.95	0.46	0.95	0.84	0.53	0.79	1.04	0.54	—	—	—	—
17	1.29	—	0.17	1.05	—	—	0.34	0.41	0.59	0.36	0.26	0.22	—	—

CONTINUE ...

CONTINUED, NRL 82-10

CARB# \ TRUE Z ->														
18	—	—	—	—	—	—	—	0.23	—	—	0.21	—	—	—
19	—	0.72	—	0.41	—	—	—	0.30	—	—	—	0.25	—	0.11
20	—	—	—	0.56	—	0.14	0.46	—	0.11	—	—	—	—	—
21	—	—	—	—	—	—	—	—	—	—	—	—	—	—
22	—	—	—	—	—	—	—	0.20	—	—	0.09	—	—	—
23	—	—	—	—	—	—	—	—	—	—	—	—	—	—
24	—	—	—	—	—	—	—	—	—	—	—	—	—	—
25	—	—	—	—	—	—	—	0.25	—	—	—	—	—	—
SUM	13.51	14.86	8.27	6.49	12.25	11.67	2.51	21.76	3.92	1.25	0.94	2.46	—	0.11

EDITED VERSION OF DP0:4NR19Z.MS
SCAN: 1, 9/ 2/86 10:36

IONISATION: FI
NO. PEAKS: 40
BASE/NREF INT: 53837./ 9844.
TIC: 110536.
MASS RANGE: 78.0469 - 162.1408
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 82-12

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 83.1
NAPHTHENES: 0.6
MONOAROMATICS: 6.4
POLYAROMATICS: 9.9

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	—	—	—	—	0.30	0.13	0.10	—	—	—	—	—	—	—
10	83.11	0.19	—	—	0.31	0.08	2.90	—	—	—	—	—	—	—
11	—	—	0.43	—	1.20	0.21	0.35	0.05	—	—	—	—	—	—
12	—	—	—	—	0.23	0.50	0.10	4.63	4.06	0.24	—	0.89	—	—
SUM	83.11	0.19	0.43	—	2.05	0.92	3.45	4.68	4.06	0.24	—	0.89	—	—

EDITED VERSION OF DP0:2NR20Z.MS
SCAN: 1, 9/ 2/86 10:58

IONISATION: FI
NO. PEAKS: 96
BASE/NREF INT: 247084./ 247084.
TIC: 644688.
MASS RANGE: 57.0703 - 176.1565
RETN TIME/MISC: 0: 0/ 0/ 2/ 0

NRL SAMPLE NO. 82-13

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 48.2
NAPHTHENES: 1.7
MONOAROMATICS: 50.0
POLYAROMATICS: 0.1

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
7	0.42	—	—	—	—	—	—	—	—	—	—	—	—	—
8	1.42	0.18	—	—	0.17	0.13	—	—	—	—	—	—	—	—
9	40.14	—	—	0.07	3.27	0.97	0.08	—	—	—	—	—	—	—
10	6.09	—	—	0.91	0.16	9.27	0.30	0.03	—	—	—	—	—	—
11	0.12	—	—	0.40	29.56	3.31	0.13	—	—	—	—	—	—	—
12	—	—	—	0.10	2.34	0.19	—	0.06	—	—	—	—	—	—
13	—	—	—	—	0.16	—	—	—	—	—	—	—	—	—
SUM	48.19	0.18	—	1.49	35.66	13.87	0.51	0.10	—	—	—	—	—	—

DP0:1NR21T.MS
SCAN: 1, 5/12/87 16: 7

IONISATION: FI
NO. PEAKS: 45
BASE/NREF INT: 5128./ 3732.
TIC: 42191.
MASS RANGE: 78.0469 - 212.2504
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 82-14

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 18.7
NAPHTHENES: 70.6
MONOAROMATICS: 10.7
POLYAROMATICS: 0.0

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
10	—	0.55	3.03	—	1.38	0.55	—	—	—	—	—	—	—	—
11	4.11	11.58	14.40	0.56	2.43	1.54	—	—	—	—	—	—	—	—
12	8.10	10.55	10.86	1.13	1.28	1.38	—	—	—	—	—	—	—	—
13	4.04	6.34	4.47	1.24	0.59	0.86	—	—	—	—	—	—	—	—
14	1.20	2.00	1.58	1.04	0.36	0.35	—	—	—	—	—	—	—	—
15	1.23	0.49	0.78	—	—	—	—	—	—	—	—	—	—	—
SUM	18.68	31.52	35.13	3.96	6.04	4.67	—	—	—	—	—	—	—	—

TOTAL NORMALIZED TO 100.0, RESPONSE FACTORS INCLUDED

EDITED VERSION OF DP0:3NR22V.MS
SCAN: 1, 4/26/85 11: 3

IONISATION: FI
NO. PEAKS: 222
BASE/NREF INT: 8573./ 8573.
TIC: 185724.
MASS RANGE: 57.0703 - 316.3130
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 82-15

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 15.3
NAPHTHENES: 34.3
MONOAROMATICS: 30.5
POLYAROMATICS: 19.9

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	—	0.30	0.14	—	0.40	—	—	—	—	—	—	—	—	—
9	0.29	0.23	0.19	—	0.65	—	—	—	—	—	—	—	—	—
10	0.43	0.28	0.21	—	0.76	0.15	—	0.30	—	—	—	—	—	—
11	0.59	0.62	0.63	—	0.87	0.78	—	2.83	—	—	—	—	—	—
12	2.06	1.21	1.23	0.59	1.10	1.47	0.13	3.87	0.09	—	—	—	—	—
13	2.75	1.60	2.44	0.99	0.89	1.92	0.28	2.89	0.29	—	—	—	—	—
14	2.36	1.40	1.40	0.94	0.90	1.86	0.62	1.61	0.57	0.14	0.09	0.14	—	—
15	1.91	1.37	2.13	0.81	0.90	1.35	0.67	1.02	0.66	0.14	0.15	0.12	—	—
16	1.57	1.12	1.12	0.65	0.78	0.93	0.59	0.11	0.61	0.18	0.13	0.13	—	—

CONTINUE ...

CONTINUED, NRL 82-15

CARB# \ TRUE Z ->														
17	1.00	1.09	0.68	0.46	0.74	0.66	0.54	0.39	0.52	0.13	0.10	0.16	—	—
18	1.09	0.88	0.54	0.49	0.63	0.56	0.34	0.32	0.27	0.13	0.07	0.14	—	—
19	0.24	0.53	0.28	0.31	0.41	0.34	0.27	0.30	0.21	0.10	0.04	0.09	—	—
20	0.51	0.39	0.38	0.27	0.34	0.25	0.25	0.20	0.10	0.07	—	0.07	—	—
21	0.28	0.25	0.19	0.18	0.20	0.18	0.14	0.13	0.07	0.04	—	0.05	—	—
22	—	—	0.11	—	0.14	0.13	0.08	0.08	0.04	—	—	—	—	—
23	—	—	—	—	0.07	—	—	—	—	—	—	—	—	—
SUM	15.34	16.69	11.96	5.68	15.99	10.56	3.92	14.04	3.42	0.93	0.57	0.89	—	—

EDITED VERSION OF DP0:1NR23W.MS
SCAN: 1, 8/19/86 13:41

IONISATION: FI
NO. PEAKS: 66
BASE/NREF INT: 4072./ 2268.
TIC: 44938.
MASS RANGE: 57.0703 - 246.2347
RETN TIME/MISC: 0: 0/ 0/ 2/ 0

NRL SAMPLE NO. 82-17

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 45.3
NAAPHTHENES" 20.1
MONOAROMATICS: 29.3
POLYAROMATICS: 5.3

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	4.57	1.36	—	—	4.38	—	—	—	—	—	—	—	—	—
10	14.47	—	1.40	—	6.25	1.33	—	0.51	—	—	—	—	—	—
11	7.98	—	—	1.67	0.74	3.18	—	4.78	—	—	—	—	—	—
12	8.51	1.51	—	0.86	—	—	4.45	—	—	—	—	—	—	—
13	5.18	1.36	—	—	3.02	0.82	0.65	—	—	—	—	—	—	—
14	—	5.69	1.06	2.51	1.90	—	—	—	—	—	—	—	—	—
15	3.33	—	0.72	—	—	1.05	—	—	—	—	—	—	—	—
16	1.23	—	—	—	—	—	—	—	—	—	—	—	—	—
17	—	1.97	—	—	—	0.87	—	—	—	—	—	—	—	—
18	—	—	—	—	0.71	—	—	—	—	—	—	—	—	—
SUM	45.27	11.89	3.18	5.04	16.98	7.26	5.10	5.28	—	—	—	—	—	—

EDITED VERSION OF DP0:3NR24P.MS
SCAN: 1, 2/19/87 14: 8

IONISATION: FI
NO. PEAKS: 211
BASE/NREF INT: 14612./ 5545.
TIC: 236064.
MASS RANGE: 57.0703 - 296.3443
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

NRL SAMPLE NO. 82-33

SUMMARY OF RESULTS (MOL %)
ACYCLIC SATURATES: 15.0
NAPHTHENES: 30.5
MONOAROMATICS: 36.2
POLYAROMATICS: 18.3

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
8	0.24	—	—	—	—	—	—	—	—	—	—	—	—	—
9	—	—	0.23	—	0.12	—	—	—	—	—	—	—	—	—
10	—	0.13	0.18	—	0.31	0.24	—	0.14	—	—	—	—	—	—
11	—	0.32	0.63	—	0.40	1.91	—	1.31	—	—	—	—	—	—
12	0.97	0.45	1.76	0.35	0.82	3.28	0.17	3.32	—	—	—	—	—	—
13	5.81	2.09	0.15	0.30	1.06	3.43	0.52	2.81	0.36	0.08	—	—	—	—
14	3.54	0.34	1.95	1.09	1.03	2.79	1.21	0.22	0.67	0.21	0.15	0.08	—	—
15	0.93	1.71	1.93	1.64	1.42	2.16	1.48	0.18	0.78	0.33	0.24	—	—	—
16	0.69	1.14	1.90	1.58	1.11	2.05	1.66	1.33	0.90	0.47	0.25	—	—	—

CONTINUE ...

CONTINUED, NRL 82-33

CARB# \ TRUE Z ->														
17	0.65	0.93	1.34	0.93	0.88	1.20	0.99	0.72	0.61	0.19	—	—	—	—
18	1.06	0.95	1.38	0.78	0.81	0.89	0.85	0.53	0.28	0.12	0.08	—	—	—
19	0.38	0.73	0.99	0.22	0.57	0.15	0.58	0.35	0.25	—	—	—	—	—
20	0.34	0.66	0.72	0.14	0.10	0.64	0.43	0.39	0.07	0.16	0.06	0.07	—	—
21	0.41	0.28	0.36	0.28	0.26	0.37	0.28	0.27	0.12	0.07	0.05	—	—	—
22	—	—	—	—	—	—	—	—	0.06	0.07	—	—	—	—
SUM	15.03	9.71	13.50	7.30	8.89	19.09	8.17	11.55	4.09	1.69	0.83	0.15	—	—

[illegible]SION OF DP0:7NR26Q.MS
[illegible] 8/29/86 15:28

[illegible]ATION: FI
[illegible] PEAKS: 119
[illegible] NREF INT: 2220./ 1340.
[illegible] 55740.
MASS RANGE: 78.0469 - 358.3599
RETN TIME/MISC: 0: 0/ 0/ 14/ 0

NRL SAMPLE NO. 83-7

SUMMARY OF RESULTS (MOL %)

ACYCLIC SATURATES:	23.1
NAPHTHENES:	24.2
MONOAROMATICS:	29.5
POLYAROMATICS:	23.2

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	—	2.19	—	—	1.37	—	—	—	—	—	—	—	—	—
10	1.05	0.95	—	—	3.58	0.44	—	—	—	—	—	—	—	—
11	1.75	—	0.86	—	4.04	1.19	—	1.05	—	—	—	—	—	—
12	3.67	1.08	—	—	3.30	2.29	—	2.79	0.50	—	—	—	—	—
13	—	—	3.46	5.12	0.52	—	2.82	0.80	—	—	—	—	—	—
14	1.94	0.84	3.07	—	1.52	—	—	—	—	0.62	1.90	—	—	—
15	—	—	—	4.03	0.40	3.53	—	0.88	—	1.43	—	—	—	—
16	3.41	—	—	2.60	—	—	—	—	—	—	1.16	—	—	—
17	—	—	—	—	0.86	—	—	0.82	—	—	1.01	—	—	—

CONTINUE ...

CONTINUED, NRL 83-7

CARB# \ TRUE Z ->														
18	—	—	—	—	0.57	—	—	2.16	0.93	—	—	—	—	—
19	—	—	—	—	0.68	—	—	2.04	—	—	—	—	—	—
20	3.34	—	—	—	0.95	—	—	—	—	—	—	—	—	—
21	2.34	—	—	—	—	—	—	1.00	—	—	—	—	—	—
22	5.65	—	—	—	—	—	—	0.76	—	—	—	—	—	—
23	—	—	—	—	—	—	—	1.64	—	—	—	—	—	—
24	—	—	—	—	0.74	—	—	0.68	—	—	—	—	—	—
25	—	—	—	—	0.70	—	—	1.00	—	—	—	—	—	—
SUM	23.14	5.05	7.39	11.76	19.24	7.44	2.82	15.61	1.43	2.05	4.07	—	—	—

EDITED VERSION OF DP0:1NR27V.MS
SCAN: 1, 9/24/84 8:58

IONISATION: FI
NO. PEAKS: 87
BASE/NREF INT: 7147./ 2129.
TIC: 59708.
MASS RANGE: 57.0703 - 296.3443
RETN TIME/MISC: 0: 0/ 0/ 2/ 0

NRL SAMPLE NO. 83-14

SUMMARY OF RESULTS (MOL %)

ACYCLIC:	27.8
NAPHTHENES:	20.6
MONOAROMATICS:	30.7
POLYAROMATICS:	20.9

CARB# \ TRUE Z ->

	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-20	-22	-24
9	—	—	—	—	0.46	—	—	—	—	—	—	—	—	—
10	—	—	—	—	1.24	0.75	—	—	—	—	—	—	—	—
11	1.15	—	—	—	1.61	1.43	—	1.18	—	—	—	—	—	—
12	—	—	—	—	1.20	1.45	—	3.66	—	—	—	—	—	—
13	2.06	1.99	0.65	—	1.32	1.81	0.37	4.19	0.51	—	—	—	—	—
14	3.99	1.34	0.80	1.05	1.43	2.04	—	2.60	0.36	0.29	—	—	—	—
15	3.99	2.06	1.36	—	1.37	1.39	0.61	1.10	0.80	0.47	—	—	—	—
16	4.23	1.72	1.07	0.75	1.31	1.32	0.68	0.76	0.98	0.36	0.45	—	—	—
17	4.01	2.19	—	—	1.09	1.10	0.63	0.68	0.67	—	0.44	—	—	—
18	3.18	1.67	—	—	0.93	0.87	0.51	—	0.56	0.24	—	—	—	—
19	2.47	1.50	0.66	—	0.94	0.71	—	—	0.23	—	—	—	—	—
20	1.60	1.01	0.75	—	0.98	0.58	—	0.37	—	—	—	—	—	—
21	1.16	—	—	—	0.56	—	—	—	—	—	—	—	—	—
SUM	27.84	13.48	5.29	1.81	14.45	13.45	2.80	14.53	4.11	1.37	0.89	—	—	—

END

7-87

DTIC